Environment Canada
Conservation & Protection

Environnement Canada
Conservation et Protection

DIOXINS AND FURANS IN SEDIMENT AND FISH FROM THE VICINITY OF TEN INLAND PULP MILLS IN BRITISH COLUMBIA

F.T.S. Mah, D.D.MacDonald, S.W.Sheehan,
T.M.Tuominen and D.Valiela

May 1989

Inland Waters
Pacific and Yukon Region
Vancouver, B.C.

ERRATUM

in: Mah, F.T.S., D.D. MacDonald, S.V. Sheehan, T.M. Tuominen, and D. Valiela. 1989. Dioxins and Furans in Sediment and Fish from the Vicinity of Ten Inland Pulp Mills in British Columbia. Inland Waters, Pacific and Yukon Region, Environment Canada, Vancouver, B.C., 77 pp.

The Abstract on page ix, line 14 of text, should read "... from LD to 1185 pg per gram..." instead of "... from LD to 1181 pg per gram..."

DIOXINS AND FURANS IN SEDIMENT AND FISH FROM THE VICINITY OF TEN INLAND PULP MILLS IN BRITISH COLUMBIA

F.T.S. Mah, D.D. MacDonald, S.W. Sheehan,

T.M. Tuominen and D. Valiela

Water Quality Branch

Inland Waters

Conservation and Protection

Pacific and Yukon Region

Environment Canada

Vancouver, B.C.

May 1989

EXECUTIVE SUMMARY

Dioxins and furans are produced in the manufacture of chlorinated herbicides, in waste incineration and other combustion, in smelters where large amounts of recycled material containing chlorinated plastics are used as well as in the production of bleached pulp. Dioxins and furans are a family of 210 related compounds of varying toxicity. The most toxic of these compounds is 2,3,7,8-tetrachlorodibenzo-para-dioxin, subsequently referred to as 2,3,7,8-T^4CDD.

Due to concerns about dioxins found in bottom sediment and fish downstream of bleached pulp mills in the United States, Environment Canada and Fisheries and Oceans Canada began a program of sampling for dioxins and furans in the vicinity of pulp and paper mills in the Pacific and Yukon Region in 1988. Similar surveys are being conducted in other regions. The primary purpose of this program was to determine the levels of dioxins and furans in fish and bottom sediment and to identify the areas of contamination in the vicinity of pulp and paper mills.

During the spring of 1988 samples of bottom sediment and fish were collected from upstream and downstream of ten pulp mill effluent discharges in the interior of British Columbia. Pulp mill locations are shown on Figure 1. At most sites three composite sediment samples were collected from upstream and downstream of discharges. Composite samples are made by mixing together equal portions of several different samples and are analysed chemically as a single sample. Similarly fish were collected at each site until at least seven fish of approximately the same size were caught for each of any three species. Fish were also collected during August and September due to

insufficient catches in the spring. Both sediment and fish samples were sent to Environment Canada's National Water Quality laboratory for chemical analysis.

The bottom sediment samples were analysed for dioxins and furans, moisture content, organic carbon and particle size. The fish were skinned and a fillet of approximately the same weight from each of seven or more fish of the same species was removed and blended into a homogeneous paste. These homogeneous composite samples were analysed for moisture, fat content and dioxins and furans.

Levels of dioxins and furans in bottom sediments were below the detection limit for most of the upstream sites. The exception was the upstream site for the pulp mills at Quesnel, located downstream from Prince George on the Fraser River. The majority of sediment samples collected downstream of pulp mills showed concentrations of 2,3,7,8-tetrachlorodibenzofuran, subsequently referred to as 2,3,7,8-T4CDF. This compound is considered to be one-tenth as toxic as 2,3,7,8-T4CDD. The highest concentrations were found in the following locations:

Downstream Locations	2,3,7,8-T4CDF in parts per trillion of dry sediment	total T4CDF in parts per trillion of dry sediment
Weyerhaeuser Canada Ltd.	3168 2445	4521 3459
Crestbrook Forest Industries Ltd.	2217	3655
Fletcher Challenge Canada Ltd. Mackenzie Pulp Division	2077 1081 982	3227 1725 1570

Statistically, the concentration of T4CDF did not show any

relationship with the levels of organic carbon content or the percentage of fine particles.

Due to the mobility of the fish, differences between upstream and downstream results for dioxins and furans in fish are not as apparent as with the sediment samples. From the results it appears that the level of 2,3,7,8-T4CDF increases in fish muscle with an increase in fat concentration.

The highest levels of 2,3,7,8-T4CDD and 2,3,7,8-T4CDF in fish are shown in the following table. Other results for fish are shown in Table 5.

Locations	Fish Species	2,3,7,8-T4CDD in parts per trillion of wet weight	2,3,7,8-T4CDF in parts per trillion of wet weight
Downstream of Northwood Pulp and Timber	largescale sucker	11.7	156
	mountain whitefish	19.5	290
Upstream of the pulp mills at Quesnel	largescale sucker	25.3	392
Downstream of the pulp mills at Quesnel	largescale sucker	20.8	321
	mountain whitefish	137	1185
Downstream of Weyerhaeuser	mountain whitefish	60.9	387
	northern squawfish	59.9	704
Downstream of Power Consolidated (China) Pulp Ltd.	lake whitefish *	10.5	908
	lake whitefish *	6.6	647

* Two different composite samples of lake whitefish.

It should be noted that because of the mobility of fish and because effluent discharges may be located relatively close to one another or downstream of a series of mills, the fish results only generally indicated areas of concern. They do not identify

the specific source of dioxins and furans in many cases.

To check on the reliability of the data generated, a quality control program was implemented for the chemical analysis of dioxins and furans. The program included frequent analysis of standards of known concentration, blanks with no dioxins, repeats of samples showing high levels, replicate analyses and interlaboratory comparisons.

SOMMAIRE EXECUTIF

Les dioxines et les furannes sont des sous-produits de la fabrication d'herbicides chlorinés, de l'incinération de déchets on d'autre combustion, de fonderies qui utilisent des matériaux contenant des plastiques chlorinés et aussi de la production de pâte blanchie. Les dioxines et les furannes sont une famille de 210 substances chimiques apparentées et de toxicité variée. Le plus toxique est 2,3,7,8-tétrachlorodibenzo-para-dioxine, abréviée comme 2,3,7,8-T4CDD.

L'inquiétude causée par la présence des dioxines dans les sédiments de fond et les poissons en aval d'usines de pâte blanchie aux Etats-Unis a amené en 1988, à l'initiation d'un programme d'échantillonage autour d'usines de pâte et de papier dans la région du Pacifique et Yukon de la part d'Environnement Canada et de Pêches et Océans Canada. Le but principal de ce programme fut de détérminer les niveaux de dioxines et de furannes dans les poissons et les sédiments de fond et d'identifier les zones contaminées autour des usines de pâte et papier.

Au printemps de 1988 des sédiments de fond et des populations de poissons ont été échantillonnés en amont et an aval d'émissaires d'effluent de dix usines de pâte et papier situées à l'intérieur de la Colombie - Britannique. L'emplacement des usines est illustré sur la Figure 1. Pour la plupart des sites trois échantillons composites ont été pris en amont et en aval des émissaires. Les échantillons composites sont formés en mélangéant des parties égales de plusieurs échantillons différents et ils sont analysés chimiquement comme échantillon unique. De la même façon, les populations de poissons ont été échantillonnés à chaque site pour obtenir au moins sept poissons de plus ou moins la même taille pour chacune de trois espèces. Les populations de poissons ont été aussi échantillonées au

cours du mois d'août et de septembre, puisque la pris de poissons au printemps n'a pas été suffissante. Les analyses chimiques des échantillons de sédiment de fond et de poissons ont été faites au Laboratoire National de la Qualité de l'Eau d'Environnement Canada.

Les sédiments de fond ont été analysés pour les concentrations de dioxines et de furannes, le contenu d'humidité, le charbon organique, et la taille de grains. Les poissons ont été dépouillés de leur peau et un filet de poids comparable de chacun de sept ou plus de poissons de la même espèce a été enlevé et homogenisé. Ces échantillons composites homogenisés ont été analysés pour l'humidité, les matières grasses, les dioxines et les furannes.

Les niveaux de dioxines et de furannes dans les sédiments de fond sont inférieures à la limite de détection (LD) dans la plupart des sites en amont des usines. L'exception fut le site en amont des usines de pâte à Quesnel et situé en aval de Prince George dans le fleuve Fraser. La plupart des échantillons de sédiments de fond en aval des usines de pâte contiennent des concentrations de 2,3,7,8-tetrachlorodibenzofuranne (2,3,7,8-T4CDF). Cette substance chimique est considerée dix fois moins toxique que 2,3,7,8-T4CDD. Les concentrations les plus hautes ont été trouvées dans les sites suivants:

Sites en aval	2,3,7,8-T4CDF en parties par trillion de sédiment sec	T4CDF totale en parties par trillion de sédiment sec
Weyerhaeuser Canada Ltd.	3168 2445	4521 3459
Crestbrook Forest Industries Ltd.	2217	3655
Fletcher Challenge Canada Ltd. Mackenzie Pulp Div.	2077 1081 982	3227 1725 1570

Statistiquement, la concentration de la T4CDF n'a montré aucune relation avec le contenu de charbon organique ou le pourcentage de particules fines.

A cause de la mobilité des poissons, les différences entre les données d'en amont et en aval des concentrations de dioxines et de furannes dans les poissons ne sont pas aussi marquées que dans les sédiments de fond. Les résultats semblent indiquer que les niveaux de 2,3,7,8-T4CDF dans les muscles des poissons augmentent avec le contenue de matiéres grasses.

Les plus hauts niveaux de 2,3,7,8-T4CDD et 2,3,7,8-T4CDF dans les poissons sont donnés dans la table suivante. D'autre résultats pour les poissons sont présentés à la Table 5.

Sites	Espèces de Poisson	2,3,7,8-T4CDD en partie par trillion de tissue humide	2,3,7,8-T4CDF en partie par trillion de tissue humide
En aval de Northwood Pulp and Timber	meunier à grandes écailles	11.7	156
	corégone des montagnes	19.5	290
En amont des usines de pâte à Quesnel	meunier à grandes écailles	25.3	392
En aval des usines de pâte à Quesnel	meunier à grandes écailles	20.8	321
	corégone des montagnes	137	1185
En aval de Weyerhaeuser	corégone des montagnes	60.9	387
	cyprinoide d'Orégon	59.9	704
En aval de Power Consolidated (China) Pulp Ltd.	grande corégone *	10.5	908
	grande corégone *	6.6	647

* Deux échantillons composites différents de grande corégone.

C'est à noter qu'à cause de la mobilité des poissons et parce que les émissaires d'effluents peuvent, quelquefois, se trouver près de l'un et de l'autre ou en aval d'une série d'usines, les résultats des poissons n'indiquent que généralement les zones d'inquiétude. Ils n'identifient pas la source spécifique des dioxines et des furannes en plusieurs cas.

Afin de vérifier la fiabilité des données obtenus, un programme de contrôles de qualité d'analyse chimique de dioxines et de furannes fut exécuté. Cela a inclus des analyses fréquentes de solution de norme à concentration connu, des échantillons blancs sans dioxines, de repetitions d'échantillons de valeurs élevées, de reproduction d'analyses et de comparaisons entre laboratoires.

Dioxins and Furans in Sediment and Fish From the Vicinity of Ten Inland Pulp Mills in British Columbia

ABSTRACT

Bed sediments and fish were collected upstream and downstream of ten pulp mills in the interior of British Columbia and analysed for dioxins and furans. The results showed that dioxin and furan concentrations in bed sediments collected downstream of pulp mills varied from less than detection limit (LD) to 4521 pg per gram of dry weight for total tetrachlorordibenzofuran (T4CDF). Bed sediments collected upstream of mills had undetectable levels of dioxins and furans, with the exception of one site. Fish samples (generally composed of composites of muscle tissue from seven fish) exhibited higher levels of dioxins and furans in fish collected downstream than upstream of the mills. The downstream samples showed dioxin concentrations from LD to 137 pg per gram wet weight for tetrachlorodibenzo-para-dioxin (T4CDD) and furans from LD to 1181 pg per gram wet weight of total T4CDF. The levels of dioxins found in upstream samples varied from LD to 25.3 pg per gram wet weight for total T4CDD while furans ranged from LD to 399 pg per gram wet weight for total T4CDF. Highest levels of dioxins and furans were found in whitefish (Prosopium williamsoni and Coregonus clupeaformis) and squawfish (Ptychocheilus oregonensis). There was a significant positive correlation between furan concentration and lipid content of fish muscle tissue.

RÉSUMÉ

Les sédiments de fond et les populations de poissons ont été échantillonnés en amont et en aval de dix usines de pâte et papier situées à l'intérieur de la Colombie-Britannique afin d'analyser leur concentration de dioxines et de furannes. Les résultats montrent que les sédiments de fond en aval des usines de pâte et papier contiennent des dioxines et surtout des furannes dont les concentrations varient d'inférieures à la limite de détection (LD) jusqu'à 4521 pg de tetrachlorodibenzofuranne (T4CDF) total par gramme de sédiment sec. Les sédiments de fond échantillonnés en amont des usines ont pour leur part des concentrations de furannes et de dioxines inférieures à la limite de détection à l'exception d'un seul site.

Chaque échantillon de poissons analysé est généralement formé de muscles de sept poissons. Ces échantillons ont des niveaux plus élevés de dioxines et de furannes dans les poissons pêchés en aval des usines (dioxines varient de la LD à 137 pg tétrachlorodibenzo-para-dioxine (T4CDD) total par gramme de tissu humide; les furannes varient de la LD à 1185 pg T4CDF total par gramme de tissu humide) que dans les poissons pêchés en amont (les dioxines varient de la LD à 25.3 pg T4CDD total par gramme de tissu humide tandis que les furannes varient de la LD à 399 pg T4CDF total par gramme de tissu humide). On retrouve les plus grandes concentrations de dioxines et de furannes dans les corégones (Prosopium williamsoni et Coregonus clupeaformis) et le Cyprinoïde d'Orégon (Ptychocheilus oregonensis). Des corrélations positives existent entre la concentration des furannes et la quantité de lipide dans les tissus musculaires des poissons.

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	i
SOMMAIRE EXECUTIF	v
ABSTRACT	ix
RÉSUMÉ	x
TABLE OF CONTENTS	xi
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
ACKNOWLEDGEMENTS	xv
INTRODUCTION	1
METHODS	3
Sampling Locations and Timing	3
Sediment Sampling	18
Fish Sampling	22
Fish Preparation	22
Age Determination of the Fish	23
Sediment Particle Size Distributions	24
Particulate Organic Carbon Determinations	24
Lipids in Fish	24
Determination of Dioxins and Furans	24
RESULTS AND DISCUSSION	27
Bed Sediments	27
Fish	40
REFERENCES	53

TABLE OF CONTENTS (CONTINUED)

	Page
APPENDIX I	55
APPENDIX II	69

LIST OF TABLES

		Page
Table 1.	Locations of Fish Sampling Sites	19
Table 2.	Specific Sampling Locations, Sampling Dates and Particle Sizes of Bed Sediment Samples.	28
Table 3.	Dioxin and Furan Residues, Organic Carbon Content and Moisture Content of Bed Sediments Collected Upstream and Downstream of Pulp Mills.	35
Table 4.	Descriptions of Fish Samples Used for Dioxins and Furans Analyses.	41
Table 5.	Dioxin and Furan Residues, Lipid Content and Moisture Content of Muscle Tissue from Fish collected Upstream and Downstream of Pulp Mills.	46
Table Ia.	Windows and Ions Used in Dioxins and Furans Analysis.	58
Table IIa.	Analytical Quality Control Results for Dioxin Analyses on Bed Sediments, Expressed as Percent Recovery.	71
Table IIb.	Analytical Quality Control Results for Dioxin Analyses on Fish Muscle Tissue, Expressed as Percent Recovery.	73
Table IIc.	Results of Replicate Bed Sediment Samples.	76
Table IId.	Results of Replicate Fish Muscle Tissue Samples.	77

LIST OF FIGURES

		Page
Figure 1.	Locations of Ten Pulp Mill Areas Studied.	4
Figure 2.	Locations of Fish and Sediment Sampling Sites near Finlay Forest Industries and Fletcher Challenge Canada Ltd.	6
Figure 3.	Locations of Fish and Sediment Sampling Sites near Northwood Pulp and Timber Ltd. and Canfor Prince George Pulp and Paper Mills.	8
Figure 4.	Locations of Fish and Sediment Sampling Sites near Quesnel River Pulp Co. and Cariboo Pulp and Paper Co.	10
Figure 5.	Locations of Fish and Sediment Sampling Sites near Weyerhaeuser Canada Ltd.	12
Figure 6.	Locations of Fish and Sediment Sampling Sites near Power Consolidated (China) Pulp Inc.	14
Figure 7.	Locations of Fish and Sediment Sampling Sites near Crestbrook Forest Industries Ltd.	16
Figure 8.	Schematic Diagram of Analytical Procedure for Polychlorinated Dioxins and Dibenzofurans.	25

ACKNOWLEDGEMENTS

The authors would like to thank G. Moyle, Water Quality Branch, for her assistance in planning, organizing and participating in field surveys; C. Baldazzi and M. Sekela of the Water Quality Branch for participating in field surveys and preparing fish samples and data tables; and B. McNaughton for formatting and editing the final report in a short time span.

We would like to thank the following agencies and individuals for their analytical work: the National Water Quality Laboratory, Burlington, Ontario, particularly, M. Forbes, J. Carron, A. Cassista, G. Jamro, J. Kohli, D. Leger and C. Young; the Fish Age Determination Unit, Pacific Biological Station, Department of Fisheries and Oceans (DFO), Nanaimo; M. Nassichuk, DFO, Vancouver for funding the fish ageing work; Sediment Laboratory, Water Resources Branch, New Westminster, especially C. Penner; Water Quality Branch Analytical Laboratory, Pacific and Yukon Region, particularly W. Cheng.

The following assisted and advised during the study: G. Kan, E. Michnowsky, N. Rousseau, S. Smith, N. Wade and P. Whitfield of the Water Quality Branch; D. Boak, Water Planning and Management Branch; G. Skitsko; DFO office at Prince George, particularly B. MacDonald and R. Elson; D. Frederic of the Fort George Band; Water Resources sub-office in Prince George; DFO office at Kamloops; S. and D. Tait, Scottie's Marina Ltd., Castlegar; A. McLean, Castlegar; J. Oliver, B.C. Ministry of Environment and Parks (MOEP), Cranbrook; B.C. MOEP regional offices in Prince George, Williams Lake, Kamloops and Cranbrook.

We would like to thank all of the individuals in the pulp and paper industry who provided assistance and advice to facilitate the collection of samples.

Finally, we would like to acknowledge the support and encouragement provided by L. Churchland, Chief, Water Quality Branch, Pacific and Yukon Region and E. Clark, Director, Inland Waters, Pacific and Yukon Region.

INTRODUCTION

Polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are produced mainly as a result of human activities. They are a by-product of the manufacture of chlorinated herbicides (Woolson et al. 1972), in the combustion of domestic and industrial wastes (Olie et al. 1977), and in smelters where large amounts of recycled material containing polyvinyl chlorides or polychlorinated paraffins are used (Marklund et al. 1986). In addition the U.S. Environmental Protection Agency National Dioxin Study (USEPA 1987), found 2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-T4CDD) to be present in fish collected downstream of some pulp and paper mills. Subsequently 2,3,7,8-T4CDD as well as 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-T4CDF) were found in bleached kraft pulp and paper mill effluent and sludges (Amendola 1987).

An Environment Canada Dioxin Task Force was formed in October 1987. The mandate of this group was to examine current information on the significance of dioxin and furan releases from the Canadian pulp and paper industry and to assess and recommend on options for their control. During 1988 the Task Force, together with the Provinces, Fisheries and Oceans Canada and Health and Welfare Canada developed a national program to sample sediment and fish in the vicinity of bleached kraft mill effluent discharges.

In January 1988, prior to the development of the national program, Environment Canada and Fisheries and Oceans Canada began a program for sampling dioxins and furans in the vicinity of pulp and paper mills in the Pacific and Yukon Region. The primary purpose of this regional program was to determine levels of dioxins and furans in fish and sediment in the vicinity of pulp and paper mills and to identify areas of contamination. In this program, Inland Waters had the responsibility of sampling

the interior mills while Environmental Protection, together with Fisheries and Oceans Canada, sampled the coastal mills. Here we report on samples collected in the vicinity of eight B.C. interior mills that utilize the chlorine bleached kraft process, as well as two thermo-mechanical pulp mills.

METHODS

Sampling Locations and Timing

Samples of bed sediments and fish were collected in the vicinity of the ten pulp mills shown in Figure 1. For each pulp mill site, sampling was conducted upstream and downstream of the mill effluent. The upstream samples were taken as far as was considered necessary from each specific site to avoid all known potential sources of dioxins and furans (i.e. other pulp mills upstream, wood treatment facilities using chlorophenols). It was not always possible to collect fish successfully at such preferred upstream sites; therefore, upstream sampling locations varied from a few hundred metres to approximately 100 km upstream of the effluent discharge. The exact locations of sediment and fish sampling for each pulp mill area are shown in Figures 2 through 7. Upstream fish sampling stations were recognized to have limited value as control stations, since even resident fish have the potential to move considerable distances. Thus fish collected upstream of effluents could have previously spent varying periods of time downstream of effluents, and vice versa. Downstream sampling was conducted at locations expected to be most affected by effluent.

Sediment sampling was conducted in the pre-freshet period (March through May) to avoid the expected loss of fine sediments and associated organic contaminants from the river beds during high flow. Fish were sampled at the same time as the sediments. At

Figure 1. Locations of Ten Pulp Mill Areas Studied

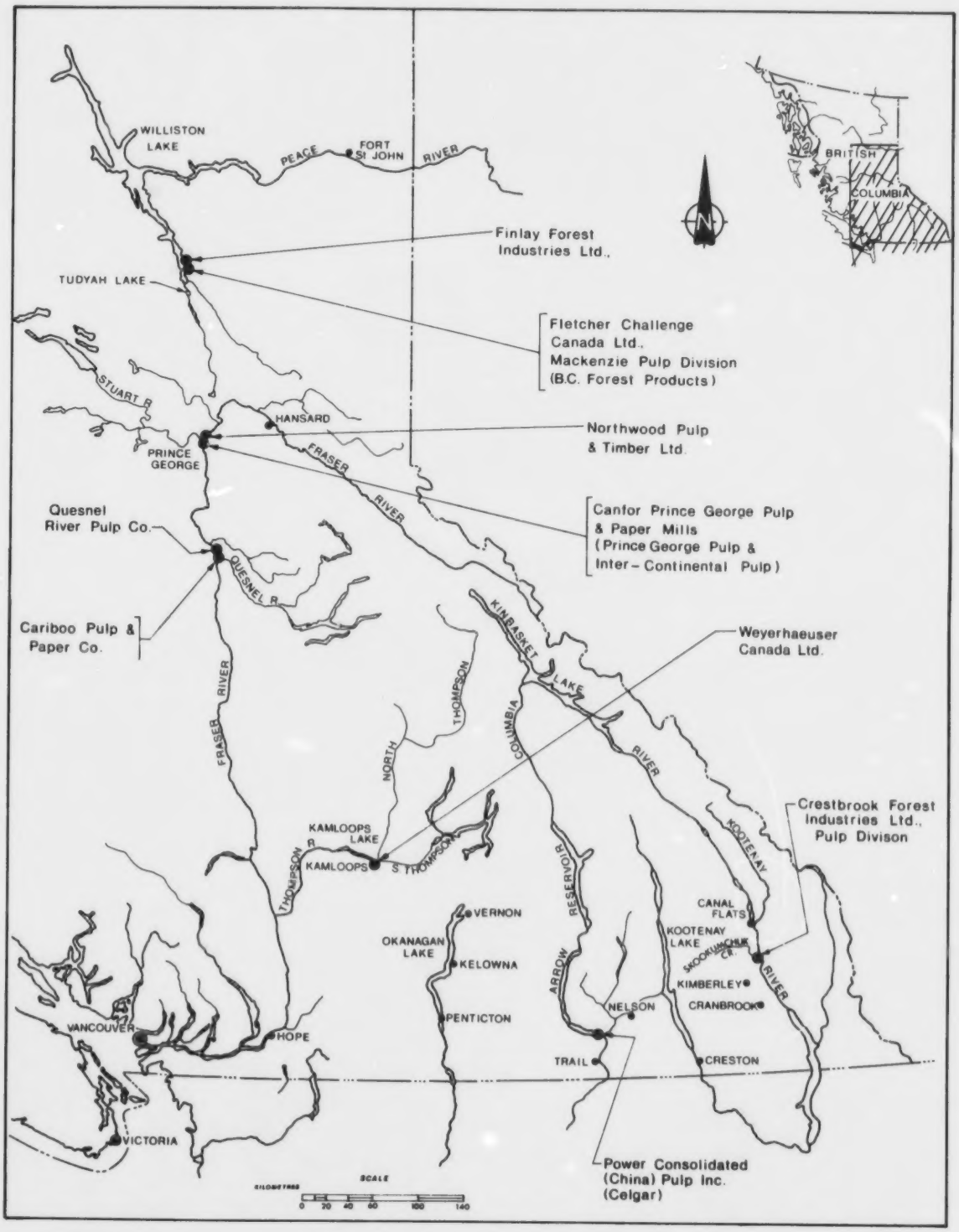

WILLISTON LAKE
PEACE
FORT St JOHN
RIVER
BRITISH COLUMBIA
N
Finlay Forest Industries Ltd.,
TUDYAH LAKE
Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (B.C. Forest Products)
STUART R
HANSARD
Northwood Pulp & Timber Ltd.
PRINCE GEORGE
FRASER RIVER
Quesnel River Pulp Co.
Canfor Prince George Pulp & Paper Mills (Prince George Pulp & Inter-Continental Pulp)
QUESNEL R
Cariboo Pulp & Paper Co.
KINBASKET LAKE
Weyerhaeuser Canada Ltd.
FRASER RIVER
NORTH THOMPSON
COLUMBIA RIVER
KAMLOOPS LAKE
KAMLOOPS
S THOMPSON
THOMPSON R
KOOTENAY
Crestbrook Forest Industries Ltd., Pulp Divison
CANAL FLATS
VERNON
OKANAGAN LAKE
KELOWNA
KOOTENAY LAKE
SKOOKUMCHUK CR.
ARROW RESERVOIR
KIMBERLEY
CRANBROOK
PENTICTON
NELSON
VANCOUVER
HOPE
TRAIL
CRESTON
VICTORIA
SCALE
KILOMETRES
0 20 40 60 100 140
Power Consolidated (China) Pulp Inc. (Celgar)

Figure 2. Locations of Fish and Sediment Sampling Sites near Finlay Forest Industries and Fletcher Challenge Canada Ltd.

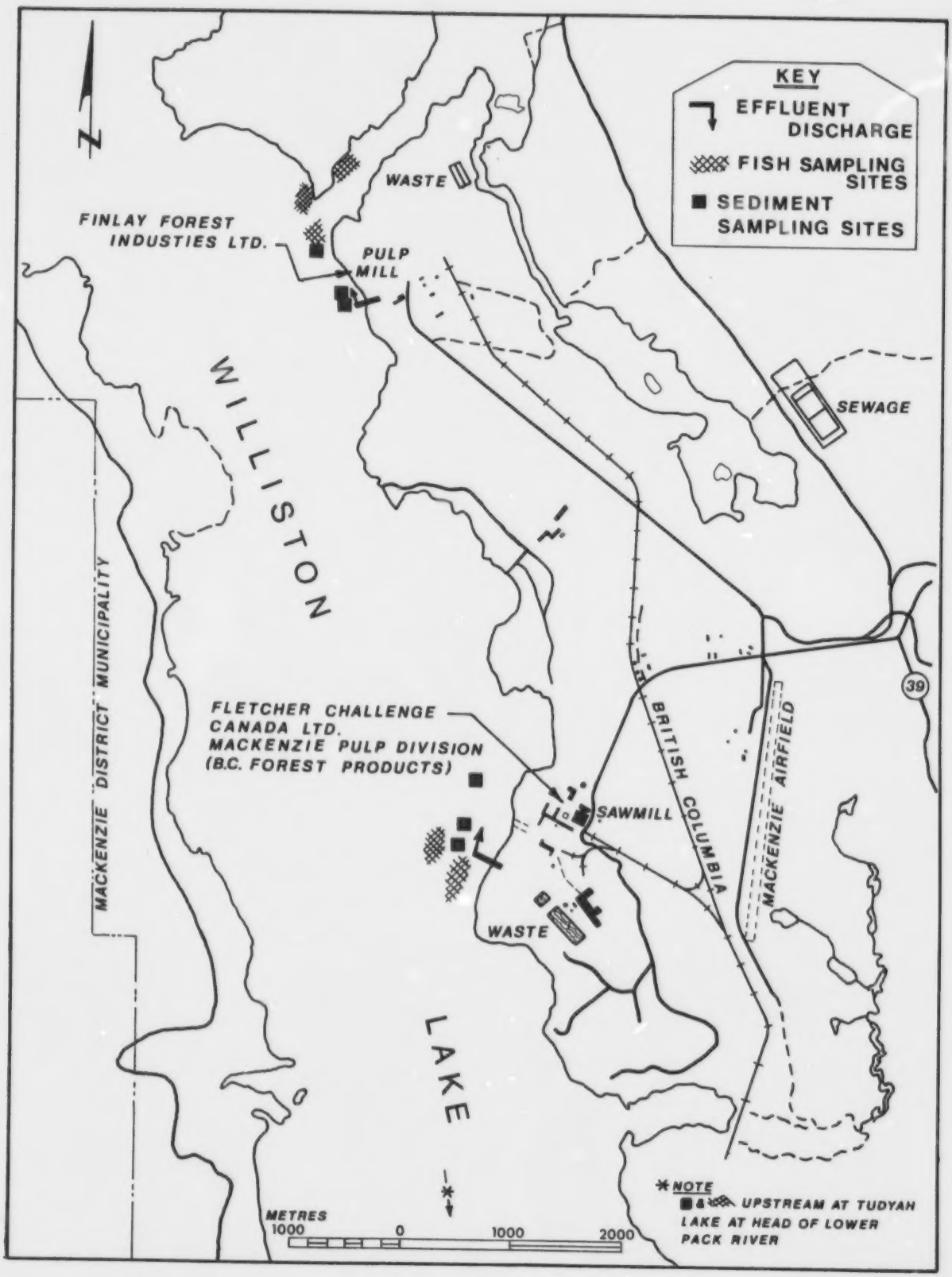

KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
N
WASTE
FINLAY FOREST INDUSTIES LTD.
PULP MILL
WILLISTON
SEWAGE
MACKENZIE DISTRICT MUNICIPALITY
FLETCHER CHALLENGE CANADA LTD. MACKENZIE PULP DIVISION (B.C. FOREST PRODUCTS)
BRITISH COLUMBIA
MACKENZIE AIRFIELD
39
SAWMILL
WASTE
LAKE
METRES
1000 0 1000 2000
*NOTE
UPSTREAM AT TUDYAH LAKE AT HEAD OF LOWER PACK RIVER

Figure 3. Locations of Fish and Sediment Sampling Sites near Northwood Pulp and Timber Ltd. and Canfor Prince George Pulp and Paper Mills.

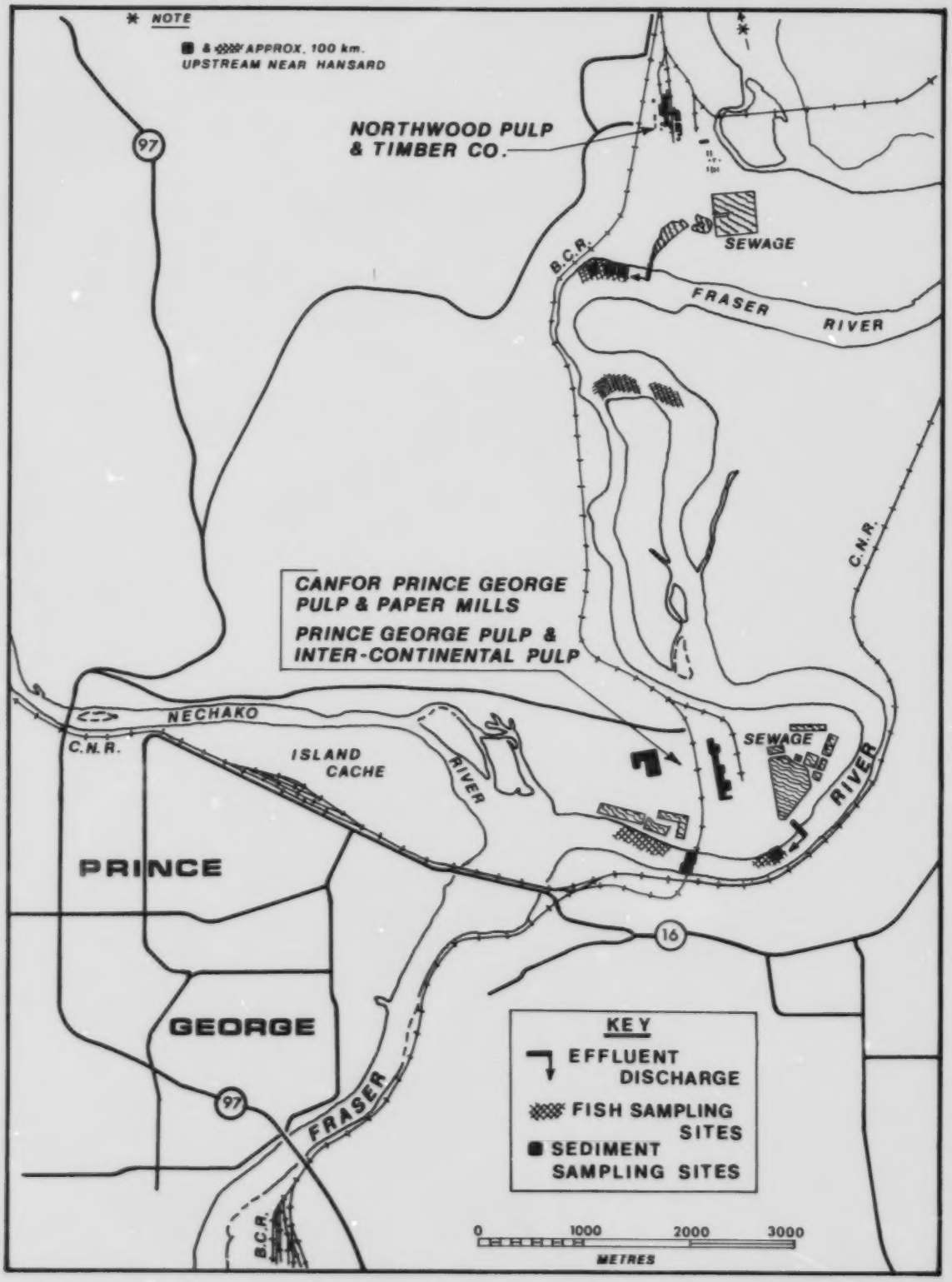

* NOTE
■ & ▨ APPROX. 100 km. UPSTREAM NEAR HANSARD
NORTHWOOD PULP & TIMBER CO.
97
B.C.R.
SEWAGE
FRASER RIVER
C.N.R.
CANFOR PRINCE GEORGE PULP & PAPER MILLS
PRINCE GEORGE PULP & INTER-CONTINENTAL PULP
NECHAKO
C.N.R.
ISLAND CACHE
RIVER
SEWAGE
RIVER
PRINCE
16
GEORGE
97
FRASER
B.C.R.
KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
0 1000 2000 3000
METRES

Figure 4. Locations of Fish and Sediment Sampling Sites near Quesnel River Pulp Co. and Cariboo Pulp and Paper Co.

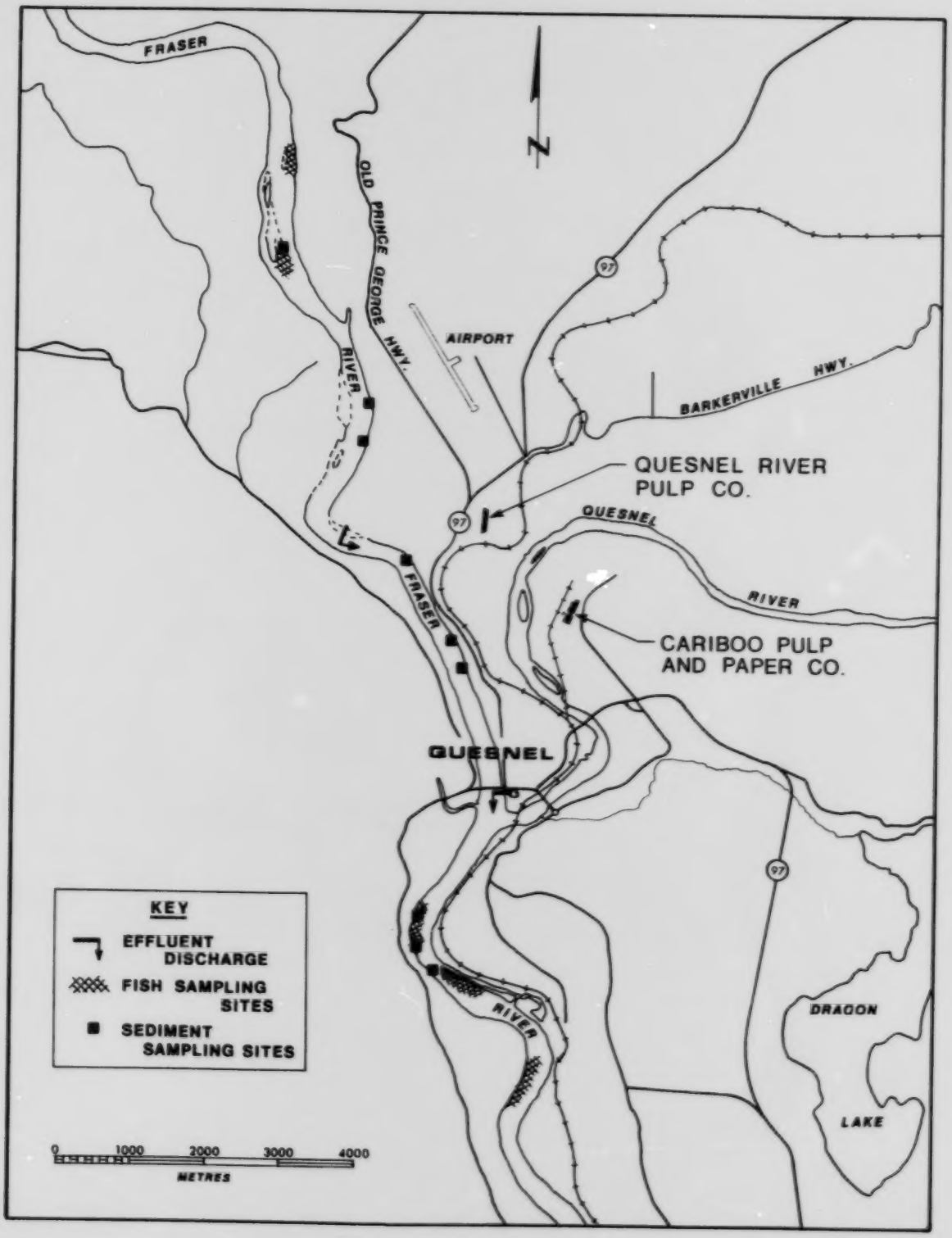

FRASER
OLD PRINCE GEORGE HWY.
RIVER
AIRPORT
97
BARKERVILLE HWY.
QUESNEL RIVER
PULP CO.
QUESNEL
RIVER
FRASER
CARIBOO PULP
AND PAPER CO.
QUESNEL
97
RIVER
DRAGON
LAKE
KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
0 1000 2000 3000 4000
METRES

Figure 5. Locations of Fish and Sediment Sampling Sites near Weyerhaeuser Canada Ltd.

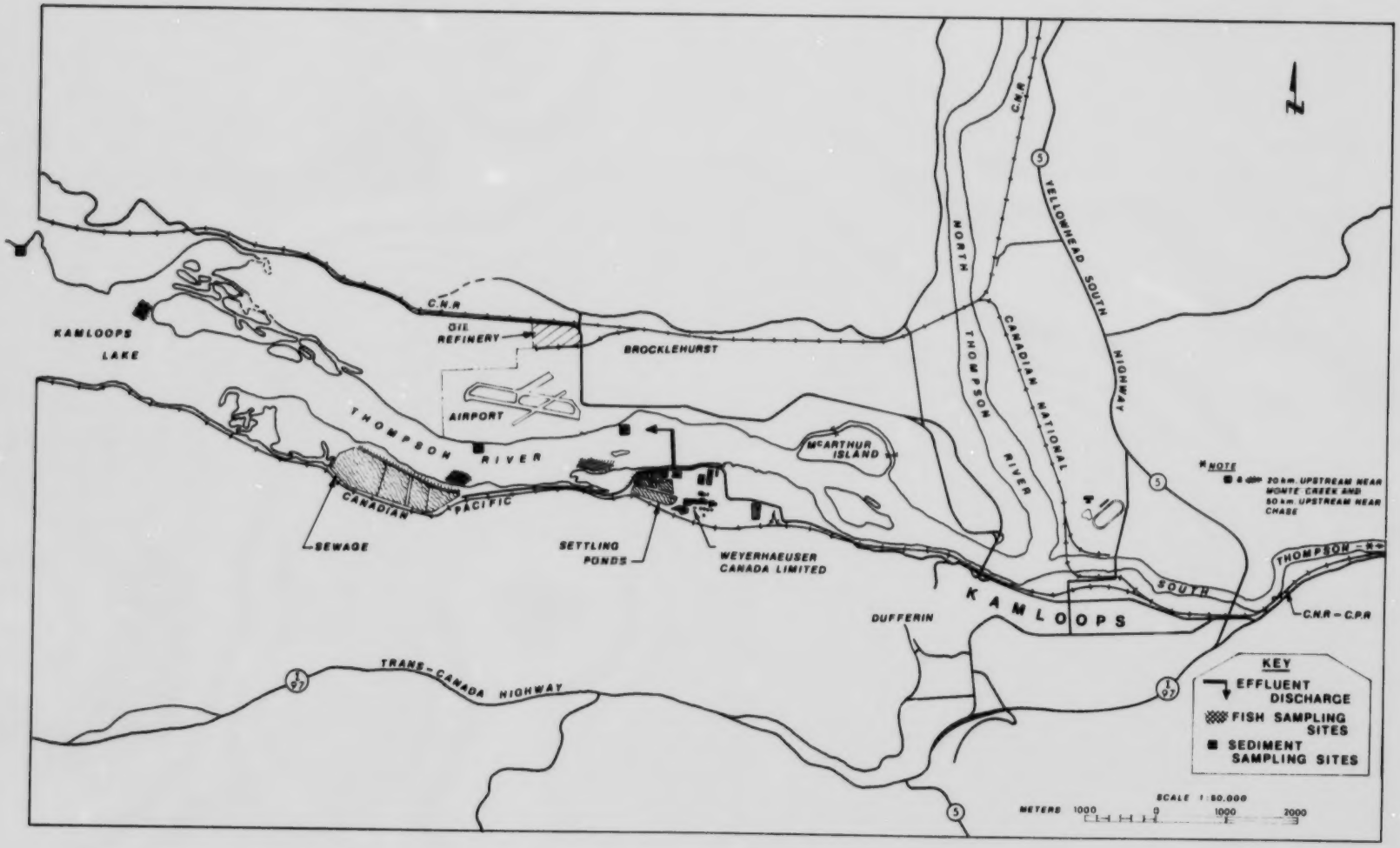

KAMLOOPS LAKE
C.N.R.
OIL REFINERY
BROCKLEHURST
AIRPORT
THOMPSON RIVER
McARTHUR ISLAND
CANADIAN PACIFIC
SEWAGE
SETTLING PONDS
WEYERHAEUSER CANADA LIMITED
NORTH THOMPSON RIVER
C.N.R.
CANADIAN NATIONAL
YELLOWHEAD SOUTH HIGHWAY
NOTE
20 km. UPSTREAM NEAR MONTE CREEK AND 50 km. UPSTREAM NEAR CHASE
THOMPSON
SOUTH
C.N.R. - C.P.R.
KAMLOOPS
DUFFERIN
TRANS-CANADA HIGHWAY
KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
METERS 1000 0 1000 2000
SCALE 1:50,000

Figure 6. Locations of Fish and Sediment Sampling Sites near Power Consolidated (China) Pulp Inc.

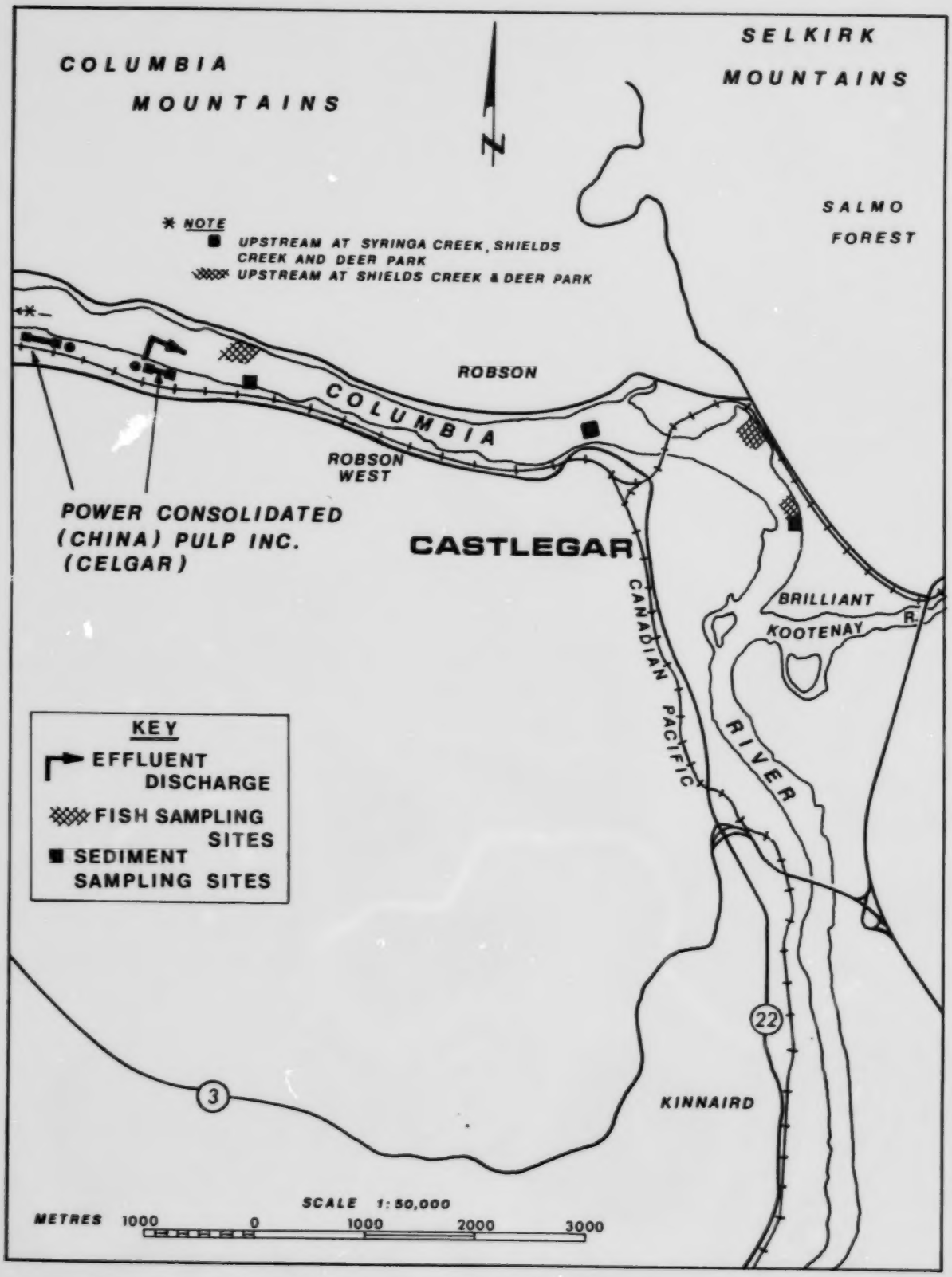
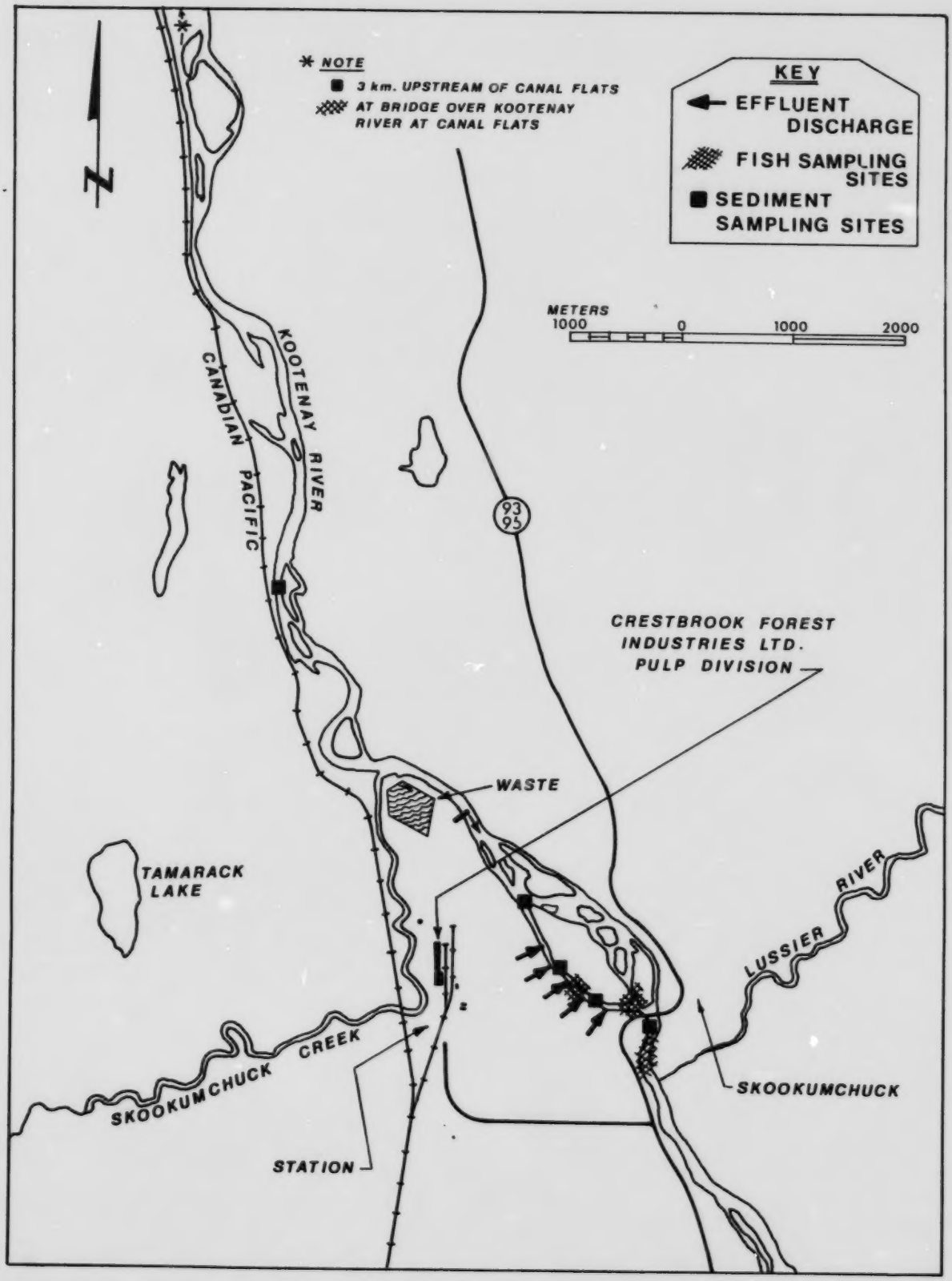

COLUMBIA
MOUNTAINS
SELKIRK
MOUNTAINS
N
SALMO
FOREST
* NOTE
UPSTREAM AT SYRINGA CREEK, SHIELDS CREEK AND DEER PARK
UPSTREAM AT SHIELDS CREEK & DEER PARK
ROBSON
COLUMBIA
ROBSON WEST
POWER CONSOLIDATED (CHINA) PULP INC. (CELGAR)
CASTLEGAR
BRILLIANT
KOOTENAY
R.
CANADIAN PACIFIC
RIVER
KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
22
3
KINNAIRD
SCALE 1:50,000
METRES 1000 0 1000 2000 3000

Figure 7. Locations of Fish and Sediment Sampling Sites near Crestbrook Forest Industries Ltd.


* NOTE
3 km. UPSTREAM OF CANAL FLATS AT BRIDGE OVER KOOTENAY RIVER AT CANAL FLATS
KEY
EFFLUENT DISCHARGE
FISH SAMPLING SITES
SEDIMENT SAMPLING SITES
METERS
1000 0 1000 2000
N
KOOTENAY RIVER
CANADIAN PACIFIC
93 95
CRESTBROOK FOREST INDUSTRIES LTD. PULP DIVISION
WASTE
TAMARACK LAKE
LUSSIER RIVER
SKOOKUMCHUCK CREEK
SKOOKUMCHUCK
STATION

each site, fish sampling continued until at least seven fish of approximately the same size were collected for each of any three species. Some locations (Fraser River by Quesnel, Columbia River by Castlegar and Kootenay River by Skookumchuk) were also sampled for fish in August and September because fish catches in the earlier samplings were not sufficient. Details of the fish sampling locations, dates and methods are presented in Table 1.

Sediment Sampling

With the exception of the Ekman and Ponar dredges, sampling equipment for dioxins/furans was cleaned as follows: (1) washed with tap water and laboratory detergent; (2) rinsed with tap water and deionized water (18 meg-ohm); (3) rinsed with pesticide grade acetone, hexane, dichloromethane, and hexane, respectively; (4) air dried and heated to 325 C for six hours. All cleaned equipment was wrapped in heat treated (325 C) aluminum foil until required. Prior to sampling, all equipment used was rinsed with water from the sample collection site.

Sediment samples were collected with a solvent (acetone, hexane, dichloromethane, hexane) rinsed Ekman dredge, Ponar sampler or stainless steel ladle and put into a stainless steel tray with a minimal amount of mixing. The top 3 to 4 cm. of the sediment sample was transferred to a stainless steel bucket with a stainless steel spoon. After collecting a minimum of three grabs in the stainless steel bucket, the composite sample was mixed well and subsamples were dispensed into Teflon jars for dioxin/furan analysis, polyethylene bottles for particle size and glass jars for particulate organic carbon determinations. The subsamples for dioxins/furans and particulate organic carbon analyses were frozen and the subsamples for particle size were kept cool.

TABLE 1. LOCATIONS OF FISH SAMPLING SITES

SITE LOCATION	GENERAL LOCATION	SPECIFIC SITE	SAMPLING DATE	SAMPLING METHOD
Mackenzie Pulp Mills Upstream	Tudyah Lake, 30 km south of Mackenzie	north end of lake, at Pack River outlet	25/05/88	gill nets 6.3 cm*
Finlay Forest Industries Ltd. Downstream	Williston Lake, Mackenzie	downstream of discharge, to entrance of cove on right bank	17/05/88 18/05/88 19/05/88	gill nets 6.3, 7.6, 11.4 cm
Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (B.C. Forest Products) Downstream	Williston Lake, Mackenzie	near discharge booms	20/05/88	gill nets 6.3, 11.4 cm
Prince George Pulp Mills Upstream	Fraser River, Hansard	boat launch site downstream of bridge, right bank	20/04/88	beach seine
	"	stream mouths and backwater at railway bridge and boat launch site	21/04/88	gill nets 6.3 cm
	"	near boat launch site downstream of railway bridge, on right bank	21/04/88	beach seine
	"	mouths of streams and backwater, at railway bridge and boat launch site	22/04/88	gill nets 6.3, 11.4 cm beach seine
	"	backwater area and stream mouth by bridge	22/04/88	gill nets 6.3 cm
Northwood Pulp and Timber Downstream	Fraser River, Prince George	30 m downstream of discharge, right bank	11/04/88	beach seine
	"	downstream, around bend, mainly in backwaters	12/04/88	beach seine

TABLE 1 (CONTINUED)

SITE LOCATION	GENERAL LOCATION	SPECIFIC SITE	SAMPLING DATE	SAMPLING METHOD
Canfor Prince George Pulp and Paper Mills Downstream	Fraser River, Prince George	right bank near old discharge site	07/04/88	beach seine
	"	right bank by old discharge site, mouth of warm water stream	08/04/88 09/04/88	gill nets 6.3, 11.4 cm beach seine
	"	between the old discharge and mouth of Nechako River, right bank	08/04/88	beach seine
Quesnel Pulp Mills Upstream	Fraser River, upstream of pulp mills	4 km upstream of Quesnel River Pulp	28/03/88	beach seine
			27/09/88	gill nets 3.8, 6.3 cm beach seine
Quesnel River Pulp Co. and Cariboo Pulp & Paper Downstream	Fraser River, downstream of Quesnel pulp mills	4-5 km downstream of Cariboo Pulp & Paper	28/03/88 27/09/88	beach seine gill nets 3.8, 6.3 cm
Weyerhaeuser Canada Ltd. Upstream	S. Thompson River, upstream of Weyerhaeuser	outlet of Shuswap Lake to 2 km downstream	21/03/88	beach seine
	"	Little Shuswap Lake	21/03/88	gill nets 6.3, 11.4 cm
Weyerhaeuser Canada Ltd. Downstream	Thompson River, at Kamloops	from Weyerhaeuser diffusers to 0.5 km below sewage treatment plant	21/03/88	beach seine
	"	Thompson River inlet to Kamloops Lake	21/03/88	gill nets 6.3, 11.4 cm
Power Consolidated (China) Pulp Inc., (Celgar) Upstream	lower Arrow Lake, upstream of Power Consolidated Pulp	mouth of Deer Creek, off Deer Park and off Renata	16/08/88	gill nets 3.8, 6.3, 11.4 cm
	"	mouth of Deer Creek, off Deer Park	17/08/88 18/08/88	gill nets 3.8, 6.3, 11.4 cm

TABLE 1 (CONTINUED)

SITE LOCATION	GENERAL LOCATION	SPECIFIC SITE	SAMPLING DATE	SAMPLING METHOD
Power Consolidated (China) Pulp Inc., (Celgar) Downstream	Columbia River, near Castlegar	600 m downstream of discharge	16/08/88 17/08/88	gill nets 6.3, 11.4 cm
	"	between public boat launch and ferry	18/08/88	beach seine
	"	600 m downstream of discharge to public boat launch	19/08/88	gill nets 6.3, 11.4 cm
Crestbrook Forest Industries Ltd., Pulp Division Upstream	Kootenay River, upstream of Crestbrook Forest Industries	1 km downstream of Canal Flats to Skookumchuk Creek	25/08/88	beach seine
	"	mouth of Skookumchuk Creek	25/08/88	beach seine
Crestbrook Forest Industries Ltd., Pulp Division Downstream	Kootenay River	downstream of Skookumchuk Bridge (Hwy 95)	14/03/88	beach seine
	"	side channel where effluent is discharged, mouth to 0.5 km upstream	14/03/88	gill nets 6.3, 11.4 cm beach seine
	"	from Skookumchuk Bridge to 1 km downstream	23/08/88	beach seine
	"	from Skookumchuk Bridge to 200 m downstream	24/08/88 25/08/88	gill nets 6.3, 11.4 cm
	"	1-2.5 km downstream of Skookumchuk Bridge	25/08/88	beach seine

* denotes gill net mesh size (diagonal).

Fish Sampling

Fish were collected by beach seine and sinking, floating and/or drifting gill nets (with mesh sizes from 3.8 cm to 11.4 cm). Captured fish were placed into stainless steel buckets or basins (rinsed for each site with a solvent series as described in the sediment sampling section) and kept cool until processed.

Field processing of the fish commenced as soon as possible after collection. Processing involved assigning labels to the fish, recording the species and length of each fish and wrapping each fish in aluminum foil (pretreated by heating to 325 C for six hours). The fish were then frozen with dry ice and kept frozen until dissection and homogenization at the laboratory.

Fish Preparation

At the laboratory, composite samples were prepared for each of three species from each sampling site. All fish in the composite sample were collected during one sampling trip; for example, fish collected in late summer were not composited with fish collected in spring. Whenever possible, the composite samples consisted of seven fish of approximately the same size. Occasionally it was not possible to collect this number for the composite; in other instances fish were small and more than seven fish had to be used for the composite to obtain enough tissue for analysis.

Prior to dissection, the fish were thawed, weighed and re-identified to confirm field identifications. The fish were skinned and epaxial muscle was removed and placed into a Teflon or glass container. Within each composite sample, approximately the same weight of tissue was removed from each fish and all the tissue was placed into the same container. The tissue was then homogenized with a Polytron ultrasonic dispersator or a blender followed by an ultrasonic dispersator until the tissue had the

consistency of fine uniform paste. The tissue was kept cool by refrigerating the tissue, the ultrasonic dispersator and the blender, except during homogenizing. For each sample, composite liver and kidney samples were similarly prepared for future analyses. The homogenized tissues were frozen in Teflon bottles.

Scales, otoliths, pectoral fins and pelvic fins were removed and retained from each fish for age determination. Prior to dissection, scales were removed from above and below the lateral line. Following dissection the pelvic fins were removed, and the head was retained for removal of attached pectoral fins and otoliths.

The equipment and containers used for fish preparation were modified and/or cleaned to prevent contamination of samples. The ultrasonic dispersator had Teflon bearings and the blender was equipped with Teflon gaskets. All equipment and containers used for the fish preparation and the Teflon sample storage bottles were washed with soap and water, rinsed with deionized water and rinsed with a solvent series (acetone, hexane, dichloromethane) prior to each use. Following this cleaning procedure, containers, storage bottles and dissecting tools were heated at 325 C for six hours. The fish were dissected on a Teflon sheet cleaned in the same manner.

Age Determination of the Fish

The ages of the fish were determined by examining annuli present in the scales, otoliths and sectioned pectoral and pelvic fins using methods described in Chilton and Beamish (1982). The ages are estimates, because the accuracy of age determinations for these species has not been validated by ageing studies. The analysis was conducted at the Fish Age Determination Unit, Department of Fisheries and Oceans, Pacific Biological Station, Nanaimo, B.C.

Sediment Particle Size Distributions

Particle size distributions were determined by hydrometer, bottom withdrawal or sieve analysis methods using procedures described in Environment Canada (1988a).

Particulate Organic Carbon Determinations

Sediment samples were dried at 100 C overnight and then pulverized in a shatter box (Spex Ind. Inc.). Inorganic carbon was removed by suspending the pulverized sediment in 0.3% (V/V) sulphuric acid for 30 minutes. The acid sediment mixture was filtered and washed with deionized water. Then the sediment was transferred to a Petri dish and dried in a heated vacuum dessicator at 65-70 C overnight. Approximately 1 mg of dried residue was weighed and pressed into a capsule with a hand press. The resultant capsule was analyzed using a Model 240XA Elemental Analyzer. The method was identical to NAQUADAT 06903 (Environment Canada 1979; 1988b) except that the dried, acid washed sediment was pressed into a capsule and no catalyst was added.

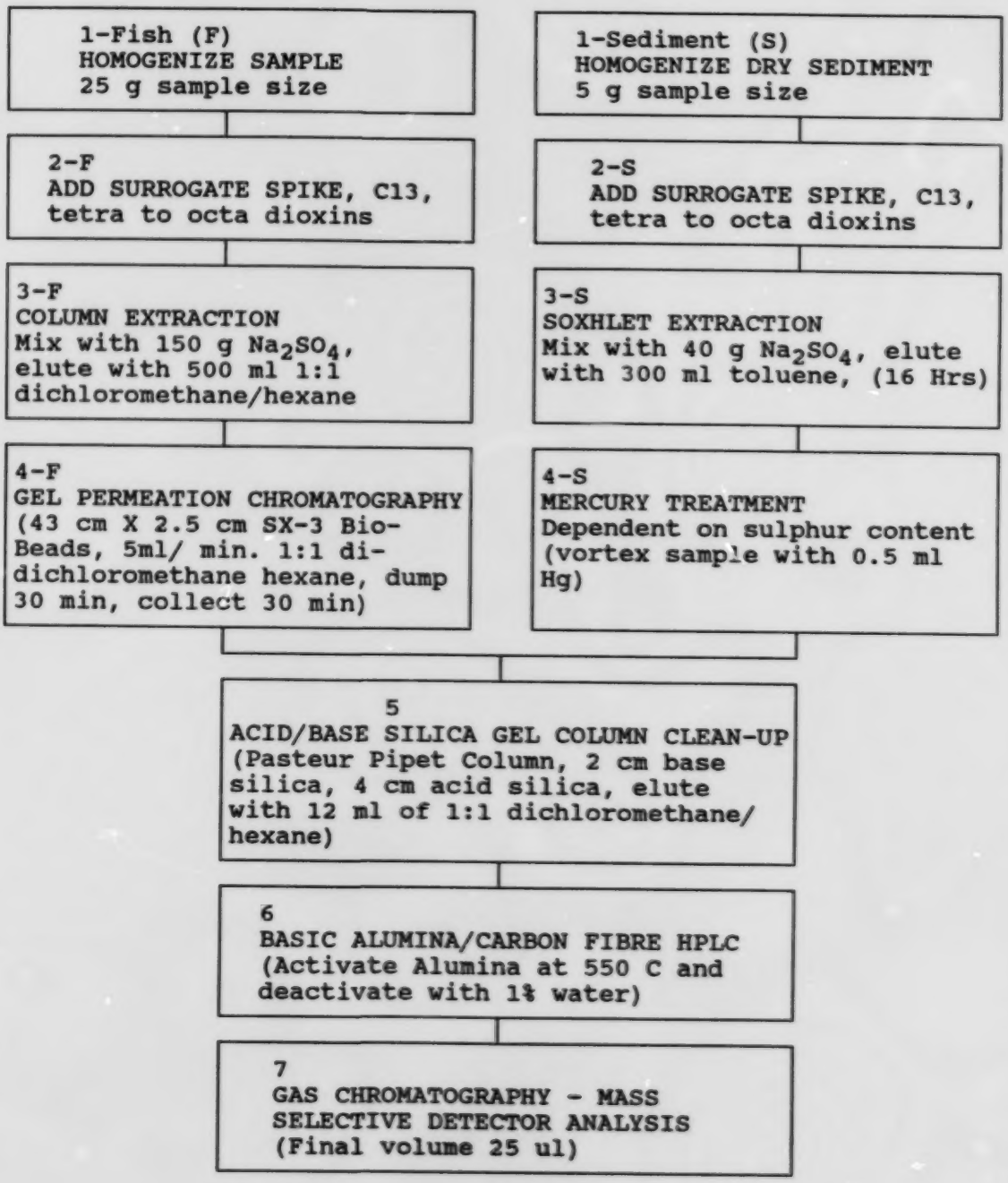
Lipids in Fish

The lipid content was determined by extracting the fish sample with 50% dichloromethane/hexane as described in section 7.2.1 of Appendix I.

Determination of Dioxins and Furans

Figure 8 summarizes the analytical method used for the analysis of dioxins and furans in sediment and fish. Appendix I describes in detail the analytical procedure used. The sediment samples were not sieved after air drying, due to difficulties

Figure 8. SCHEMATIC DIAGRAM OF ANALYTICAL PROCEDURE FOR POLYCHLORINATED DIOXINS AND DIBENZOFURANS


1-Fish (F)
HOMOGENIZE SAMPLE
25 g sample size
1-Sediment (S)
HOMOGENIZE DRY SEDIMENT
5 g sample size
2-F
ADD SURROGATE SPIKE, C13, tetra to octa dioxins
2-S
ADD SURROGATE SPIKE, C13, tetra to octa dioxins
3-F
COLUMN EXTRACTION
Mix with 150 g Na_2SO_4, elute with 500 ml 1:1 dichloromethane/hexane
3-S
SOXHLET EXTRACTION
Mix with 40 g Na_2SO_4, elute with 300 ml toluene, (16 Hrs)
4-F
GEL PERMEATION CHROMATOGRAPHY (43 cm X 2.5 cm SX-3 Bio-Beads, 5ml/ min. 1:1 di-dichloromethane hexane, dump 30 min, collect 30 min)
4-S
MERCURY TREATMENT
Dependent on sulphur content (vortex sample with 0.5 ml Hg)
5
ACID/BASE SILICA GEL COLUMN CLEAN-UP (Pasteur Pipet Column, 2 cm base silica, 4 cm acid silica, elute with 12 ml of 1:1 dichloromethane/ hexane)
6
BASIC ALUMINA/CARBON FIBRE HPLC (Activate Alumina at 550 C and deactivate with 1% water)
7
GAS CHROMATOGRAPHY - MASS SELECTIVE DETECTOR ANALYSIS
(Final volume 25 ul)

experienced in sieving sediments containing large amounts of fibrous material. Instead, the samples were mixed with a spatula. Quality assurance and quality control for the dioxin-/furan determinations are presented in Appendix II.

RESULTS AND DISCUSSION

Bed Sediments

Table 2 presents the particle sizes of the bed sediment samples. Most samples consisted predominantly of sand or sand and silt; variability in the proportions of different size categories is evident between samples within one site and between locations. The concentrations of dioxins and furans in the sediment samples, as well as moisture content and organic carbon content are presented in Table 3.

The levels of all dioxins and furans were below detection limit for most of the upstream sites. The exception was the upstream site for the pulp mills at Quesnel. One of the three samples collected upstream of these pulp mills had levels of 2,3,7,8-T4CDF and total T4CDF similar to or greater than levels measured in two of the six samples collected downstream of the pulp mills at Quesnel. The upstream site for Quesnel is located on the Fraser River and is downstream of discharges from pulp mills at Prince George. Thus, the Prince George effluents can contaminate sediments upstream of Quesnel.

The majority of sediments collected downstream of the pulp mills contained 2,3,7,8-T4CDF and total T4CDF. In addition, sediments collected downstream of Finlay Forest Industries contained pentachlorodibenzo-para-dioxins (P5CDD) and octachlorodibenzo-para-dioxins (O8CDD). Sediments collected in the vicinity of Fletcher Challenge Canada Ltd., Mackenzie Pulp Division, also showed levels of O8CDD as well as pentachlorodibenzofurans (P5CDF), hexachlorodibenzofurans (H6CDF) and heptachlorodibenzofurans (H7CDF). The presence of O8CDD indicates another

TABLE 2. SPECIFIC SAMPLING LOCATIONS, SAMPLING DATES AND PARTICLE SIZES OF BED SEDIMENT SAMPLES

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Mackenzie Pulp Mills Upstream	Tudyah Lake, 20 m from right bank, near source of Pack River	05/25/88	1.0	91.6	4.2	3.2
	Tudyah Lake, mid-channel, near source of Pack River	05/25/88	0.4	86.7	8.6	4.3
	Tudyah Lake, 20 m from left bank, near source of Pack River	05/25/88	0.3	90.4	5.4	3.9
Finlay Forest Industries Ltd. Downstream	0.5-3 m from discharge in Williston Lake	05/17/88	0.0	92.7	5.8	1.5
	20 m from discharge in Williston Lake	05/17/88	0.0	71.6	21.0	7.4
	500 m from discharge in Williston Lake	05/17/88	0.0	3.0	66.7	30.3
Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (B.C. Forest Products) Downstream	20 m from discharge in Williston Lake	05/18/88	0.8	27.4	51.8	20.0
	200 m from discharge in Williston Lake	05/19/88	0.0	2.9	77.4	19.7
	600 m from discharge in Williston Lake	05/19/88	0.0	8.9	69.2	21.9

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Prince George Pulp Mills Upstream	Hansard, Fraser River, 250 m downstream of railway bridge, 0.75 to 1 m depth	04/20/88	0.0	45.2	46.7	8.1
	Hansard, Fraser River, 600 m downstream of railway bridge, 0.75 m depth	04/20/88	1.9	33.6	56.2	8.3
	Hansard, Fraser River, 1 km downstream of railway bridge, right bank	04/20/88	2.2	5.8	54.8	37.2
Northwood Pulp and Timber Downstream	Fraser River, 250 m downstream of discharge, right bank	04/11/88	0.2	33.2	60.9	5.7
	Fraser River, 300 m downstream of discharge, right bank	04/11/88	0.0	60.2	34.8	5.0
	Fraser River, 500 m downstream of discharge, right bank	04/11/88	0.1	55.9	38.5	5.5

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Canfor Prince George Pulp and Paper Mills Downstream	Fraser River, 350 m downstream of discharge at 2 m depth, right bank	04/06/88	0.2	53.6	40.4	5.8
	Fraser River, 1.2 km downstream of discharge under the railway bridge, 2nd abutment from left bank	04/07/88	0.5	67.3	27.0	5.2
	Fraser River, 1.2 km downstream of discharge under the railway bridge, 3rd abutment from left bank	04/07/88	0.0	86.9	9.1	4.0
Quesnel Pulp Mills Upstream	Fraser River, 3.5 km upstream of Quesnel River Pulp Co. discharge, left bank	03/28/88	1.4	57.9	33.2	7.5
	Fraser River, 2 km upstream of Quesnel River Pulp Co. discharge, left bank	03/28/88	0.0	68.7	26.0	5.3
	Fraser River, 1.3 km upstream of Quesnel River Pulp Co. discharge, left bank	03/28/88	27.2	46.5	14.3	12.0

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Quesnel River Pulp Co. Downstream	Fraser River, 650 m downstream of discharge, left bank	03/28/88	9.8	49.2	33.5	7.5
	Fraser River, 2 km downstream of discharge, left bank	03/28/88	0.9	89.9	5.8	3.4
	Fraser River, 2.5 km downstream of discharge, left bank	03/28/88	0.3	26.6	61.7	11.4
Cariboo Pulp and Paper Downstream	Fraser River, 2 km downstream of Cariboo discharge, right bank	03/28/88	0.3	44.0	46.5	9.2
	Fraser River, 2.2 km downstream of Cariboo discharge, right bank	03/28/88	0.8	47.2	42.3	9.7
	Fraser River, 2.6 km downstream of Cariboo discharge, right bank	03/28/88	1.4	59.5	28.3	10.8

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Weyerhaeuser Canada Ltd. Upstream	S. Thompson River, 10-30 m downstream of Chase Bridge	03/22/88	8.2	73.1	13.3	5.4
	S. Thompson River, 1 km west of Monte Creek	03/22/88	1.2	88.2	7.3	3.3
	S. Thompson River, upstream of Weyerhaeuser fresh water intake	03/22/88	1.9	67.9	25.4	4.8
Weyerhaeuser Canada Ltd. Downstream	Thompson River, 200 m downstream of north bank diffuser	03/22/88	0.4	97.1	2.5 **	
	Thompson River, 2.3 km downstream of north bank diffuser, 100 m from last sewage lagoon of Kamloops STP, north shore	03/22/88	0.5	96.1	3.4 **	
	Thompson River, 8 km downstream of north bank diffuser, across from railway tunnel, north shore	03/22/88	0.0	86.6	10.4	3.0

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Power Consolidated (China) Pulp Inc., (Celgar) Upstream	Arrow Lake, at mouth of Deer Creek	03/17/88	0.9	95.0	4.1 **	
	Arrow Lake, at mouth of Shield Creek	03/17/88	1.5	95.2	3.3 **	
	Arrow Lake, at mouth of Syringa Creek	03/17/88	1.6	52.5	39.2	6.7
Power Consolidated (China) Pulp Inc., (Celgar) Downstream	Columbia River, 300 m downstream of discharge	03/17/88	0.0	59.5	37.3	3.2
	Columbia River, 800 m downstream of discharge	03/17/88	0.0	39.6	55.0	5.4
	Columbia River, 1.3 km downstream of discharge	03/17/88	0.1	58.9	37.2	3.8

TABLE 2 (CONTINUED)

SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	PARTICLE SIZE *			
			% GRAVEL	% SAND	% SILT	% CLAY
Crestbrook Forest Industries Ltd., Pulp Division Upstream	Kootenay River, 3 km upstream of Canal Flats, east bank	03/14/88	0.0	65.9	27.9	6.2
	Kootenay River, 2.5 km upstream of mill	03/14/88	0.0	73.2	21.4	5.4
Crestbrook Forest Industries Ltd., Pulp Division Downstream	Kootenay River, where discharge and ground water seep to surface	03/14/88	0.0	37.5	54.0	8.5
	Kootenay River, 300 m downstream of previous site	03/14/88	0.0	73.2	20.9	5.9
	Kootenay River, 300 m downstream of previous site	03/14/88	0.0	63.3	34.7	2.0
	Kootenay River, below effluent pipe which is used only during high flow conditions	03/14/88	0.0	59.4	28.2	12.4

* particle size categories are defined as follows: gravel = 2-64 mm, sand = 0.062-2 mm, silt = 0.004-0.062 mm, clay = <0.004 mm

** refers to % particle size of silt & clay combined

TABLE 3. DIOXIN AND FURAN RESIDUES, ORGANIC CARBON CONTENT AND MOISTURE CONTENT OF BED SEDIMENTS COLLECTED UPSTREAM AND DOWNSTREAM OF PULP MILLS

SAMPLING LOCATION	MOISTURE CONTENT (%)	ORGANIC C (mg/g)	DIOXIN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Mackenzie Pulp Mills	27.3	4.2	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Upstream	33.4	4.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	31.0	5.1	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Finlay Forest Industries	83.1	240.0	L15	L15	28	L30	L50	94	L10	19.4	L15	L25	L40	L75
Downstream	89.2	167.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	70.3	59.0	L15	L15	L20	L30	L50	206	286	672	L15	L25	L40	L75
Fletcher Challenge Canada Ltd.	62.1	106.0	L15	L15	L20	L30	L50	572	2077	3227	51	34	L40	L75
Mackenzie Pulp Division (B.C. Forest Products)	60.0	58.0	L15	L15	L20	L30	L50	100	982	1570	L15	L25	L40	L75
Downstream	51.3	44.0	L15	L15	L20	L30	L50	L75	1081	1725	L15	L25	(7.4)	L75
Prince George Pulp Mills	37.5	5.2	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Upstream	41.0	9.7	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	28.6	8.7	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75

TABLE 3 (CONTINUED)

SAMPLING LOCATION	MOISTURE CONTENT (%)	ORGANIC C (mg/g)	DIOXIN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Northwood Pulp and Timber	48.0	12.0	L15	L15	L20	L30	L50	L75	274	406	L15	L25	L40	L75
Downstream	39.0	6.8	L15	L15	L20	L30	L50	L75	69.9	101	L15	L25	L40	L75
	39.0	6.4	L15	L15	L20	L30	L50	L75	44.6	67.4	L15	L25	L40	L75
Canfor Prince George Pulp and Paper Mills	32.9	4.2	L15	L15	L20	L30	L50	L75	50.7	77.5	L15	L25	L40	L75
Downstream	35.6	4.7	L15	L15	L20	L30	L50	L75	63.7	63.7	L15	L25	L40	L75
	27.7	1.5	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Quesnel Pulp Mills	34.2	2.2	L15	L15	L20	L30	L50	L75	134	192	L15	L25	L40	L75
Upstream	27.5	1.7	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	18.6	1.5	L15	L15	L20	L30	L50	L75	36.8	54.9	L15	L25	L40	L75
Quesnel River Pulp Co.	64.1	24.0	L15	L15	L20	L30	L50	L75	238	359	L15	L25	L40	L75
Downstream	30.5	2.2	L15	L15	L20	L30	L50	L75	36.6	53.8	L15	L25	L40	L75
	59.6	25.0	L15	L15	L20	L30	L50	L75	213	315	L15	L25	L40	L75

TABLE 3 (CONTINUED)

SAMPLING LOCATION	MOISTURE CONTENT (%)	ORGANIC C (mg/g)	DIOXIN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Cariboo Pulp and Paper Downstream	41.7	5.8	L15	L15	L20	L30	L50	L75	195	281	L15	L25	L40	L75
	43.2	7.6	L15	L15	L20	L30	L50	L75	159	232	L15	L25	L40	L75
	36.5	[illegible]7	L15	L15	L20	L30	L50	L75	120	176	L15	L25	L40	L75
Weyerhaeuser Canada Ltd. Upstream	54.7	7.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	32.2	2.7	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	33.1	3.7	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Weyerhaeuser Canada Ltd. Downstream	32.4	12.0	L15	L15	L20	L30	L50	L75	3168	4521	L15	L25	L40	L75
	46.5	11.0	L15	L15	L20	L30	L50	L75	2445	3459	L15	L25	L40	L75
	30.2	2.8	L15	L15	L20	L30	L50	L75	68.5	96.7	L15	L25	L40	L75
Power Consolidated (China) Pulp Inc. (Celgar) Upstream	24.0	2.9	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	26.8	1.4	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	35.9	9.2	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Power Consolidated (China) Pulp Inc. (Celgar) Downstream	78.1	210.0	L15	L15	L20	L30	L50	L75	642	642	L15	L25	L40	L75
	58.0	47.0	L15	L15	L20	L30	L50	L75	298	330	L15	L25	L40	L75
	39.8	11.0	L15	L15	L20	L30	L50	L75	100	125	L15	L25	L40	L75

TABLE 3 (CONTINUED)

SAMPLING LOCATION	MOISTURE CONTENT (%)	ORGANIC C (mg/g)	DIOXIN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Crestbrook Forest Industries Ltd., Pulp Division Upstream	39.2	54.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
	33.8	47.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75
Crestbrook Forest Industries Ltd., Pulp Division Downstream	76.0	130.0	L15	L15	L20	L30	L50	L75	2217	3655	L15	L25	L40	L75
	37.6	42.0	L15	L15	L20	L30	L50	L75	77.9	116	L15	L25	L40	L75
	50.8	42.0	L15	L15	L20	L30	L50	L75	27.4	27.4	L15	L25	L40	L75
	43.8	42.0	L15	L15	L20	L30	L50	L75	L10	L10	L15	L25	L40	L75

L denotes less than specified detection limit.
( ) denotes value was below method detection limit, however a peak was detected.

potential source of contamination as 2,3,7,8-T4CDD and 2,3,7,8-T4CDF are the principal dioxins and furans found in bleached kraft pulp and paper mill matrices (Amendola et al. 1987). Recent production batches of chlorophenols were reported to contain certain dioxins and furans principally hepta and octachloro congeners (Cull et al. 1984). Environmental Protection records (Lui 1989) show that Fletcher Challenge Canada Ltd., Mackenzie Sawmill Division, located adjacent to the pulp mill, has used chlorophenols and is thus a possible source of these congeners at these sites.

In some locations, it is not possible to determine the source of the contaminants because more than one pulp mill is located in a reach of river or lake. For example (see Figure 1), at Mackenzie on Williston Lake, Finlay Forest Industries and Fletcher Challenge Canada, Mackenzie Pulp Division, are located within 5 km of each other. At Prince George, discharges from Canfor enter the Fraser River 7 km downstream of those of Northwood. At Quesnel, Quesnel River Pulp is located 135 km downstream of the Prince George pulp mills and effluents from Cariboo Pulp and Paper enter the Fraser River 4 km downstream of Quesnel River Pulp. The results must be interpreted considering the proximity of other pulp mills in the same drainage system.

The highest levels of furans were measured in bed sediments collected downstream of Weyerhaeuser Canada Ltd. (two samples; 3168 and 2445 pg/g 2,3,7,8-T4CDF; 4521 and 3459 pg/g total T4CDF), downstream of Crestbrook Forest Industries Ltd. (2217 pg/g 2,3,7,8-T4CDF; 3655 pg/g total T4CDF), and near Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (2077 pg/g 2,3,7,8-T4CDF; 3227 pg/g total T4CDF).

The concentrations of furans measured in the downstream sediment samples were not significantly correlated with organic carbon content or with percent silt plus clay (fine particles) in the

samples. Linear regressions among these variables had low regression coefficients (R Squared < 0.02, 26 degrees of freedom (d.f.) in each of four regressions). This is in spite of the wide range of variability in organic carbon content (range 1.5 to 240 mg/g) and percent fines (range 2.5 to 97 percent; see Table 2) represented in the downstream samples. It appears that the degree of contamination of bed sediments, at least for this relatively small set of samples, was primarily determined by sample location relative to sources of contamination and was not greatly affected by organic carbon content or particle size of sediments.

Fish

The species of fish used for each composite sample, the number of fish in the sample, and the median and range of lengths, weights and ages of fish in the samples are presented in Table 4. The largescale sucker (Catostomus macrocheilus) was the only species collected that was common to all sites.

The concentrations of dioxins and furans, lipid content and moisture content are presented in Table 5. Total T4CDF and 2,3,7,8-T4CDF were detected in all fish samples collected downstream of the pulp mills. The dioxins, 2,3,7,8-T4CDD and total T4CDD, were measurable in many of the downstream samples; however they were at lower concentrations than the T4CDFs. Other congeners of dioxins and furans were present in some samples. Downstream of Northwood Pulp and Timber, P5CDF was detected; at Quesnel, upstream and downstream of the pulp mills, P5CDD, P5CDF and H6CDD were detected; downstream of Weyerhaeuser Canada Ltd., P5CDF and P5CDD were detected in one sample; and downstream of Power Consolidated (China) Pulp Inc., P5CDF was detected in one sample.

Differences between downstream and upstream data are not as apparent as with the sediment samples. This is to be expected

TABLE 4. DESCRIPTIONS OF FISH SAMPLES USED FOR DIOXINS AND FURANS ANALYSES

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) g	MEDIAN AGE (Range) years
Mackenzie Pulp Mills Upstream	25/05/88	Catostomus macrocheilus (largescale sucker)	7	343.0 (334-352)	488.7 (397.5-579.9)	10 (7-20)
		Hylocheilus caurinus (peamouth chub)	7	223.0 (205-241)	120.2 (95.2-145.2)	10 (9-13)
		Prosopium williamsoni (mountain whitefish)	7	329.5 (318-341)	394.1 (353.4-434.7)	14 (12-23)
Finlay Forest Industries Ltd. Downstream	17/05/88 18/05/88 19/05/88	Catostomus macrocheilus (largescale sucker)	7	359.0 (248-470)	874.7 (178.6-1570.8)	18 (7-20)
	17/05/88	Coregonus clupeaformis (lake whitefish)	7	312.5 (305-320)	297.0 (263.0-331.0)	10 (8-15)
	19/05/88	Lota lota (burbot)	7	393.0 * (374-412)	364.5 (297.2-431.7)	8 (6-9)
Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (B.C. Forest Products) Downstream	20/05/88	Catostomus macrocheilus (largescale sucker)	7	368.5 (288-449)	695.7 (249.8-1141.5)	16 (9-20)
		Coregonus clupeaformis (lake whitefish)	7	327.5 (319-336)	301.3 (239.1-363.4)	10 (8-17)
		Lota lota (burbot)	7	398.0 * (365-431)	371.0 (255.5-486.4)	7 (3-9)

TABLE 4 (CONTINUED)

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) g	MEDIAN AGE (Range) years
Prince George Pulp Mills Upstream	20/04/88 21/04/88 22/04/88	Catostomus catostomus (longnose sucker)	7	330.5 (310-351)	405.2 (328.3-482.0)	14 (10-18)
	20/04/88 21/04/88	Catostomus macrocheilus (largescale sucker)	7	338.5 (304-373)	412.7 (298.0-527.4)	10 (10-16)
	21/04/88 22/04/88	Ptychocheilus oregonensis (northern squawfish)	7	307.0 (275-339)	345.8 (217.2-474.4)	9 (6-12)
Northwood Pulp and Timber Downstream	11/04/88 12/04/88	Catostomus macrocheilus (a) (largescale sucker)	7	458.5 (423-494)	1197.7 (976.8-1418.6)	25 (20-32)
		Catostomus macrocheilus (b) (largescale sucker)	7	426.0 (376-476)	925.1 (575.3-1274.8)	17 (12-28)
		Prosopium williamsoni (mountain whitefish)	7	217.0 (158-276)	181.6 (33.8-329.3)	4 (2-10)
Canfor Prince George Pulp and Paper Mills Downstream	08/04/88	Catostomus columbianus (bridgelip sucker)	7	388.0 (378-398)	618.8 (505.4-732.2)	20 (17-24)
	07/04/88 08/04/88 09/04/88	Catostomus macrocheilus (largescale sucker)	6	336.5 (305-368)	410.8 (327.6-494.0)	10 (9-12)
	07/04/88 08/04/88	Prosopium williamsoni (mountain whitefish)	11	177.5 (164-191)	55.9 (40.9-70.8)	3 (3-4)

TABLE 4 (CONTINUED)

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) g	MEDIAN AGE (Range) years
Quesnel Pulp Mills Upstream	27/09/88	Catostomus columbianus (bridgelip sucker)	7	312.5 (275-350)	333.8 (210.8-456.7)	9 (6-9)
	28/03/88	Catostomus macrocheilus (largescale sucker)	7	468.5 (442-495)	1276.1 (1023.4-1528.8)	23 (18-26)
	27/09/88	Mylocheilus caurinus (peamouth chub)	12	177.5 (165-190)	59.7 (45.1-74.3)	6 (4-7)
Quesnel River Pulp Co. and Cariboo Pulp and Paper Downstream	27/09/88	Catostomus columbianus (bridgelip sucker)	7	297.5 (260-335)	301.0 (168.1-433.9)	9 (8-10)
	28/03/88	Catostomus macrocheilus (largescale sucker)	7	443.0 (380-506)	1099.3 (654.6-1543.9)	21 (11-27)
	27/09/88	Prosopium williamsoni (mountain whitefish)	7	292.5 (240-345)	275.6 (126.8-424.4)	8 (4-13)
	27/09/88	Salvelinus malma (dolly varden)	7	390.0 (300-480)	692.4 (279.1-1105.6)	6 (4-11)
Weyerhaeuser Canada Ltd. Upstream	21/03/88	Catostomus macrocheilus (largescale sucker)	7	443.5 (410-477)	1063.2 (817.4-1308.9)	22 (13-28)
		Prosopium williamsoni (mountain whitefish)	7	312.5 (301-324)	314.1 (259.6-368.6)	8 (5-9)
		Salvelinus malma (dolly varden)	7	368.0 (333-403)	651.9 (464.5-839.2)	6 (5-7)

TABLE 4 (CONTINUED)

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) g	MEDIAN AGE (Range) years
Weyerhaeuser Canada Ltd. Downstream	21/03/88	Catostomus macrocheilus (largescale sucker)	7	426.5 (408-445)	887.7 (742.2-1033.2)	22 (17-30)
		Prosopium williamsoni (mountain whitefish)	7	232.5 (170-295)	135.2 (47.5-222.8)	3 (2-8)
		Ptychocheilus oregonensis (northern squawfish)	7	424.5 (374-475)	1077.7 (658.0-1497.3)	17 (14-28)
Power Consolidated (China) Pulp Inc., (Celgar) Upstream	16/08/88 17/08/88	Catostomus macrocheilus (largescale sucker)	7	314.0 (281-347)	360.8 (224.7-496.9)	10 (9-13)
	16/08/88 17/08/88 18/08/88	Coregonus clupeaformis (lake whitefish)	7	391.0 (274-508)	1183.2 (228.5-2137.8)	6 (5-8)
	16/08/88 17/08/88	Ptychocheilus oregonensis (northern squawfish)	7	510.0 (484-536)	1999.5 (1660.4-2338.6)	16 (11-24)
Power Consolidated (China) Pulp Inc., (Celgar) Downstream	16/08/88 17/08/88 18/08/88 19/08/88	Catostomus macrocheilus (largescale sucker)	7	461.5 (440-483)	1215.3 (1115.8-1314.7)	20 (9-25)
	16/08/88	Coregonus clupeaformis (a) (lake whitefish)	7	469.5 (460-479)	1313.4 (1161.5-1465.3)	6 (5-9)
		Coregonus clupeaformis (b) (lake whitefish)	7	447.5 (440-455)	1198.1 (1057.1-1339.0)	4 (3-7)

TABLE 4 (CONTINUED)

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) g	MEDIAN AGE (Range) years
Crestbrook Forest Industries Ltd., Pulp Division Upstream	25/08/88	Catostomus macrocheilus (largescale sucker)	7	397.5 (380-415)	644.2 (548.2-740.2)	11 (10-18)
		Prosopium williamsoni (mountain whitefish)	7	267.5 (255-280)	203.6 (146.4-260.8)	6 (4-7)
		Salmo clarki (cutthroat trout)	7	261.0 (227-295)	205.0 (120.6-289.3)	3 (3-4)
Crestbrook Forest Industries Ltd., Pulp Division Downstream	24/08/88 25/08/88	Catostomus macrocheilus (a) (largescale sucker)	6	337.5 (250-425)	450.3 (158.7-741.9)	14 (6-19)
	14/03/88	Catostomus macrocheilus (b) (largescale sucker)	4	392.5 (365-420)	658.7 (484.4-832.9)	12 (10-14)
	23/08/88 24/08/88 25/08/88	Prosopium williamsoni (mountain whitefish)	7	283.0 (250-316)	207.7 (100.5-314.9)	6 (5-11)

* refers to total length rather than fork length

TABLE 5. DIOXIN AND FURAN RESIDUES, LIPID CONTENT AND MOISTURE CONTENT OF MUSCLE TISSUE FROM FISH COLLECTED UPSTREAM AND DOWNSTREAM OF PULP MILLS

SITE LOCATION	FISH SPECIES	LIPID CONTENT (%_wet_wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Mackenzie Pulp Mills Upstream	Catostomus macrocheilus (largescale sucker)	0.7	80.1	L2	L2	L3	L5	L10	L15	27.4	27.4	L3	L5	L10	L15
	Mylocheilus caurinus (peamouth chub)	1.4	79.5	3.5	3.5	L3	L5	L10	L15	84.5	84.5	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	1.8	76.3	L2	L2	L3	L5	L10	L15	25.9	25.9	L3	L5	L10	L15
Finlay Forest Industries Ltd. Downstream	Catostomus macrocheilus (largescale sucker)	2.3	78.8	3.7	3.7	L3	L5	L10	L15	48.7	48.7	L3	L5	L10	L15
	Coregonus clupeaformis (lake whitefish)	1.9	79.5	4.6	4.6	L3	L5	L10	L15	80.1	80.1	L3	L5	L10	L15
	Lota lota (burbot)	0.9	79.8	L2	L2	L3	L5	L10	L15	6.2	6.2	L3	L5	L10	L15
Fletcher Challenge Canada Ltd. Mackenzie Pulp Division (B.C. Forest Products) Downstream	Catostomus macrocheilus (largescale sucker)	1.8	79.2	2.5	2.5	L3	L5	L10	L15	40.3	40.3	L3	L5	L10	L15
	Coregonus clupeaformis (lake whitefish)	1.1	81.6	2.4	2.4	L3	L5	L10	L15	48.4	48.4	L3	L5	L10	L15
	Lota lota (burbot)	0.8	81.7	L2	L2	L3	L5	L10	L15	11.1	11.1	L3	L5	L10	L15

TABLE 5 (CONTINUED)

SITE LOCATION	FISH SPECIES	LIPID CONTENT (%_wet_wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Prince George Pulp Mills Upstream	Catostomus catostomus (longnose sucker)	0.4	81.0	L2	L2	L3	L5	L10	L15	L2	L2	L3	L5	L10	L15
	Catostomus macrocheilus (largescale sucker)	0.2	80.6	L2	L2	L3	L5	L10	L15	L2	L2	L3	L5	L10	L15
	Ptychocheilus oregonensis (northern squawfish)	0.6	80.1	L2	L2	L3	L5	L10	L15	L2	L2	L3	L5	L10	L15
Northwood Pulp and Timber Downstream	Catostomus macrocheilus (a) (largescale sucker)	1.6	79.3	11.7	11.7	L3	L5	L10	L15	156	156	L3	L5	L10	L15
	Catostomus macrocheilus (b) (largescale sucker)	0.9	79.5	5.4	5.4	L3	L5	L10	L15	85.1	85.1	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	0.8	78.2	19.5	19.5	L3	L5	L10	L15	290	290	4.0	L5	L10	L15
Canfor Prince George Pulp and Paper Mills Downstream	Catostomus columbianus (bridgelip sucker)	1.5	79.1	2.0	2.0	L3	L5	L10	L15	43.1	43.1	L3	L5	L10	L15
	Catostomus macrocheilus (largescale sucker)	0.3	81.1	L2	L2	L3	L5	L10	L15	40.8	40.8	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	0.3	79.5	4.4	4.4	L3	L5	L10	L15	67.4	67.4	L3	L5	L10	L15

TABLE 5 (CONTINUED)

SITE LOCATION	FISH SPECIES	LIPID CONTENT (%_wet_wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Quesnel Pulp Mills Upstream	Catostomus columbianus (bridgelip sucker)	0.7	78.2	L2	L2	L3	L5	L10	L15	4.2	4.2	L3	L5	L10	L15
	Catostomus macrocheilus (largescale sucker)	3.2	78.1	25.3	25.3	3.0	6.7	L10	L15	392	399	7.2	L5	L10	L15
	Mylocheilus caurinus (peamouth chub)	0.5	79.6	8.1	8.1	L3	L5	L10	L15	68.1	68.1	L3	L5	L10	L15
Quesnel River Pulp Co. and Cariboo Pulp and Paper Downstream	Catostomus columbianus (bridgelip sucker)	2.5	78.3	2.9	2.9	L3	L5	L10	L15	15.8	15.8	L3	L5	L10	L15
	Catostomus macrocheilus (largescale sucker)	3.1	77.8	20.8	20.8	3.0	9.2	L10	L15	321	327	6.1	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	5.7	75.8	137	137	12.8	40.8	L10	L15	1185	1185	25.1	L5	L10	L15
	Salvelinus malma (dolly varden)	2.0	78.8	12.4	12.4	L3	L5	L10	L15	23.8	23.8	L3	L5	L10	L15
Weyerhaeuser Canada Ltd. Upstream	Catostomus macrocheilus (largescale sucker)	3.4	79.1	L2	L2	L3	L5	L10	L15	2.0	2.0	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	2.0	78.1	L2	L2	L3	L5	L10	L15	22.4	22.4	L3	L5	L10	L15
	Salvelinus malma (dolly varden)	8.3	70.3	L2	L2	L3	L5	L10	L15	16.4	16.4	L3	L5	L10	L15

TABLE 5 (CONTINUED)

SITE LOCATION	FISH SPECIES	LIPID CONTENT (%_wet_wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Weyerhaeuser Canada Ltd. Downstream	Catostomus macrocheilus (largescale sucker)	1.8	79.9	12.5	12.5	L3	L5	L10	L15	16.0	16.0	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	1.9	79.3	60.9	60.9	L3	L5	L10	L15	387	387	L3	L5	L10	L15
	Ptychocheilus oregonensis (northern squawfish)	3.8	76.1	59.9	59.9	4.2	L5	L10	L15	704	704	12.7	L5	L10	L15
Power Consolidated (China) Pulp Inc. (Celgar) Upstream	Catostomus macrocheilus (largescale sucker)	0.6	81.5	L2	L2	L3	L5	L10	L15	2.0	2.0	L3	L5	L10	L15
	Coregonus clupeaformis (lake whitefish)	4.4	74.6	L2	L2	L3	L5	L10	L15	45.4	45.4	L3	L5	L10	L15
	Ptychocheilus oregonensis (northern squawfish)	9.2	73.1	L2	L2	L3	L5	L10	L15	5.9	5.9	L3	L5	L10	L15
Power Consolidated (China) Pulp Inc. (Celgar) Downstream	Catostomus macrocheilus (largescale sucker)	2.0	78.5	L2	L2	L3	L5	L10	L15	25.8	25.8	L3	L5	L10	L15
	Coregonus clupeaformis (a) (lake whitefish)	8.9	72.7	10.5	10.5	L3	L5	L10	L15	908	908	13.4	L5	L10	L15
	Coregonus clupeaformis (b) (lake whitefish)	10.5	72.4	6.6	6.6	L3	L5	L10	L15	647	647	L3	L5	L10	L15

TABLE 5 (CONTINUED)

SITE LOCATION	FISH SPECIES	LIPID CONTENT (% wet wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
Crestbrook Forest Industries Ltd., Pulp Division Upstream	Catostomus macrocheilus (largescale sucker)	1.1	81.5	L2	L2	L3	L5	L10	L15	L2	L2	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	3.7	75.7	L2	L2	L3	L5	L10	L15	9.8	9.8	L3	L5	L10	L15
	Salmo clarki (cutthroat trout)	1.6	77.9	L2	L2	L3	L5	L10	L15	9.1	9.1	L3	L5	L10	L15
Crestbrook Forest Industries Ltd., Pulp Division Downstream	Catostomus macrocheilus (a) (largescale sucker)	0.6	81.8	L2	L2	L3	L5	L10	L15	27.1	27.1	L3	L5	L10	L15
	Catostomus macrocheilus (b) (largescale sucker)	1.1	80.1	L2	L2	L3	L5	L10	L15	38.6	38.6	L3	L5	L10	L15
	Prosopium williamsoni (mountain whitefish)	2.0	75.1	L2	L2	L3	L5	L10	L15	25.6	25.6	L3	L5	L10	L15

L denotes less than specified detection limit.

because of the mobility of fish. Fish collected at an upstream site may have previously resided in an area affected by discharges and alternatively, fish collected in the area of a discharge may have just arrived at that site from a clean upstream location. Many of the upstream fish samples had low but measurable concentrations of dioxins and furans. Nevertheless, the concentrations found upstream were generally lower than those found at the downstream stations. A single exception was the largescale sucker sample collected upstream of the pulp mills at Quesnel, where marginally higher levels of dioxins and furans were measured in samples collected upstream of a pulp mill than in the same species collected downstream of the mill. Because the same species were not always collected upstream and downstream of the mills, only limited comparisons can be made.

The highest levels of dioxins were measured in mountain whitefish (Prosopium williamsoni) collected downstream of the pulp mills at Quesnel (137 pg/g 2,3,7,8-T4CDD), mountain whitefish collected downstream of Weyerhaeuser Canada Ltd. (60.9 pg/g 2,3,7,8-T4CDD) and northern squawfish (Ptychocheilus oregonensis) collected downstream of Weyerhaeuser (59.9 pg/g 2,3,7,8-T4CDD). The highest levels of furans were measured in the mountain whitefish sample collected downstream of the pulp mills at Quesnel (1185 pg/g 2,3,7,8-T4CDF), the northern squawfish sample collected downstream of Weyerhaeuser (704 pg/g 2,3,7,8-T4CDF), and two samples of lake whitefish (Coregonus clupeaformis) collected downstream of Power Consolidated (China) Pulp Inc. (908 and 647 pg/g 2,3,7,8-T4CDF). For all of the above samples, the concentrations of total T4CDD and T4CDF were the same as those for the respective 2,3,7,8-isomer.

The mean concentrations of 2,3,7,8-T4CDD and 2,3,7,8-T4CDF in largescale sucker collected downstream of pulp mills were, respectively, 6.1 and 80 pg/g (n = 10 in each case). For mountain whitefish, the corresponding mean concentrations were

44.6 and 391 pg/g (n = 5 in each case). For lake whitefish, the mean concentrations were 6.0 and 421 pg/g (n = 4). The single downstream composite sample of northern squawfish shows concentrations of 59.9 and 704 pg/g for the two isomers. Thus there appears to be a tendency for higher levels of dioxins and furans to be found in fish species occupying higher trophic (food web) levels such as the mountain whitefish, the northern squawfish and lake whitefish collected at stations downstream of pulp mills.

The concentrations of dioxins and furans found in fish muscle collected at downstream stations were generally not significantly correlated with either weight of fish or lipid content of muscle tissue (R Squared < 0.10, 23 d.f. in each of three regressions). The only exception was the correlation between the concentration of 2,3,7,8-TCDF (or of total T4CDF which is nearly identical) in fish muscle and its lipid content. In this case, the regression coefficient was 0.6 (23 d.f.; $P \leq 0.01$), which is a strong correlation considering the small sample size and the expected variability induced by fish movement patterns and species differences.

There was an indication of a positive correlation between fish age and content of dioxins and furans; but none of the correlations were significant at the $P \leq 0.05$ level. The strongest correlation between median fish age and content of dioxins and furans was found in the case of largescale suckers for 2,3,7,8-T4CDD (R squared = 0.48 with 8 d.f., where the 0.05 sigificance level corresponds to an R squared of 0.63). However, in most cases the sample size within a species was too small to perform credible correlation analyses.

REFERENCES

Amendola, G., D. Barna, R. Blosser, L. LaFleur, A. McBride, F. Thomas, T. Tiernan and R. Whittemore. 1987. The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills presented at Seventh International Symposium on Chlorinated Dioxins and Related Compounds; Las Vegas, Nevada, U.S.A.

Chilton, D. E. and R. J. Beamish. 1982. Age Determination Methods for Fishes Studied by the Groundfish Program at the Pacific Biological Station. Can. Spec. Publ. Fish. Aq. Sci. 60.

Cull, M.R., A.J. Dobbs, M. Goudot and N. Schultz. 1984. Polychlorodibenzo-p-dioxins and Dibenzofurans in Technical Pentachlorophenol; Results of a Collaborative Analytical Exercise. Chemosphere 13(10):1157-1165.

Environment Canada. 1979. Analytical Methods Manual, Water Quality Branch, Inland Waters Directorate, Ottawa, Canada.

Environment Canada. 1988a. Laboratory Procedures for Sediment Analysis, 2nd Edition, Sediment Survey Section, Water Resources Branch, Inland Waters Directorate, Ottawa, Canada.

Environment Canada. 1988b. NAQUADAT, Dictionary of Parameter Codes, Data Systems Section, Water Quality Branch, Inland Waters Directorate, Ottawa, Canada.

Liu, S. 1989. Program Officer for Forest Products Program. Environmental Protection, Environment Canada, West Vancouver, B.C. Personal Communication.

Marklund, S., L.O. Kjeller, M. Hansson, M. Tysklind, C. Rappe, C. Ryan, H. Collazo and R. Dougherty. 1986. Determination of PCDDs and PCDFs in Incineration Samples and Pyrolytic Products. In, C. Rappe, G. Choudhary and L.H. Keith (eds.). Chlorinated Dioxins and Dibenzofurans in Perspective. Lewis Publishers. Chelsea, Michigan, USA. pp. 79-92.

Olie, K., P.L. Vermeulen and O. Hutzinger. 1977. Chlorodibenzo-p-dioxins and Chlorodibenzofurans are Trace Components of Fly Ash and Flue Gas of Some Municipal Incinerators in the Netherlands. Chemosphere 6:455-459.

USEPA. 1987. The National Dioxin Study, Tiers 3, 5, 6 and 7. United States Environmental Protection Agency (USEPA). Office of Water Regulations and Standards; EPA 440/4-87-003.

Woolson, E.A., R.F. Thomas and P.D. Enson. 1972. Survey of Polychlorodibenzo-p-dioxin Content in Selected Pesticides. J. Agr. Food Chem. 20:351-354.

APPENDIX I

METHOD FOR DETERMINATION OF POLYCHLORINATED DIOXINS AND DIBENZOFURANS IN FISH AND SEDIMENT (GC-MS)

(Forbes 1989)

NATIONAL WATER QUALITY LABORATORY

1.0 Scope and Application

1.1 This method covers the determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in fish and sediment samples.

1.2 The following isomers can be individually quantitated:

Isomer	Detection Limit (pg/g)	
	Fish(25g)	Sediment(5g)
2,3,7,8-T4CDD and T4CDF	2	15
1,2,3,7,8-P5CDD and P5CDF	3	20
1,2,3,4,7,8-H6CDD and H6CDF	5	25
1,2,3,4,6,7,8-H7CDD and H7CDF	10	50
O8CDD and O8CDF	15	75

If other isomers are found in the sample, their concentrations are added to the corresponding individual isomer and the result is reported as total (i.e. total H6CDD).

1.3 This method can also be applied to water, sludge and pulp samples.

2.0 Summary

2.1 All samples are spiked with a mixture of five C13 labelled dioxins prior to extraction. Wet fish samples are mixed with sodium sulphate, packed in a column and extracted with 50% dichloromethane(DCM)/hexane. The extract is then subjected to gel permeation chromatography (GPC) cleanup to remove lipids. Sediment samples are dried and extracted with toluene using a soxhlet extraction apparatus.
The sample extract is passed through an acid/base silica gel column. It is then fractionated using a custom made alumina column and carbon fibre column module via high performance liquid chromatography. The resulting extract is concentrated to 25 uL and analysed by gas chromatography using a mass selective detector (MSD).

3.0 Interferences

3.1 Polychlorinated biphenyls (PCBs), naphthalenes (PCNs), diphenyl ethers (PCDPEs), xanthones, xanthenes and other chlorinated organic contaminants have been reported as potential interferences.

4.0 Sampling Procedure and Storage

4.1 Samples should be collected and stored in clean glass or Teflon containers with Teflon or aluminum lined caps.

4.2 Samples should be stored frozen.

5.0 Apparatus

5.1 Standard laboratory glassware consisting of beakers, round bottom flasks, Allihn filters, centrifuge tubes, micro vials, disposable pipets, etc.

5.2 Glass extraction columns (55 cm X 3.2 cm ID), soxhlets and heating apparatus, extraction thimbles.

5.3 Evaporator units (Pierce Reacti-Therm and Reacti-Vap heating module).

5.4 GPC system: Analytical Biochemistry Laboratories Autoprep model 1002A modified to allow total injection of samples onto loops. Column consists of 60 g SX-3 Bio-Beads (Bio-Rad Laboratories) swelled in 50% DCM/hexane, packed in 2.5 cm I.D. glass column, bed compressed to 43 cm, column eluted at 5 mL/min with 50% DCM/hexane. Dump cycle is 30 min., collect cycle is 30 min. and wash cycle is 10 min.

5.5 Stainless steel columns, 30 cm X 7.8 mm ID (Waters PN 84175), Waters model 590 programmable HPLC pump, six port valves.

5.6 Syringes.

5.7 Hewlett Packard HP 5880A gas chromatograph fitted with a 30 m X 0.20 mm I.D. X 0.11 um (thickness) HP Ultra 2 column (equivalent to DB-5). Insert end of column directly in source of HP 5970 MSD used in electron impact mode at 70 eV. Set electron multiplier at 2500 V and dwell times at 100 ms. Make injections in splitless mode using the following conditions: injector 250 C; interface 250 C; column 80 C for 3 min, 20 C/min to 180 C, 5 C/min to 260 C,

hold for 30 min.; carrier gas, helium at 15 psi head pressure.

The ions monitored and their windows are listed in Table Ia.

Table Ia. Windows and Ions used in Dioxins and Furans Analysis

Window (min)	Compound	Quantitation ion	Confirmation ions
15-18	2,3,7,8-T4CDD	322	320,259
	2,3,7,8-T4CDF	306	304,243
	C13 2,3,7,8-T4CDD	334	332
	C13 1,2,3,4-T4CDD	334	332
18-21	1,2,3,7,8-P5CDD	356	354,293
	1,2,3,7,8-P5CDF	340	338,277
	C13 1,2,3,7,8-P5CDD	368	366
21-24	1,2,3,4,7,8-H6CDD	390	392,327
	1,2,3,4,7,8-H6CDF	374	376,311
	C13 1,2,3,4,7,8-H6CDD	402	404
24-28	1,2,3,4,6,7,8-H7CDD	424	426,361
	1,2,3,4,6,7,8-H7CDF	408	410,345
	C13 1,2,3,4,6,7,8-H7CDD	436	438
28-30	O8CDD	460	458,397
	O8CDF	444	442,379
	C13 O8CDD	472	470

5.8 Polytron ultrasonic dispersator (Brinkmann Instruments).

6.0 Reagents and Standards

6.1 Dioxin and furan standards (CIL Isotopes Lab) in toluene:

A. surrogate standards: 50 pg/uL C13 2,3,7,8-T4CDD
100 pg/uL C13 1,2,3,7,8-P5CDD
100 pg/uL C13 1,2,3,4,7,8-H6CDD

100 pg/uL C13 1,2,3,4,6,7,8-H7CDD
150 pg/uL C13 O8CDD

B.performance standard: 50 pg/uL C13 1,2,3,4-T4CDD

C.quantitation standards:

50 pg/uL C13 and native 2,3,7,8-T4CDD
100 pg/uL C13 and native 1,2,3,7,8-P5CDD
100 pg/uL C13 and native 1,2,3,4,7,8-H6CDD
100 pg/uL C13 and native 1,2,3,4,6,7,8-H7CDD
150 pg/uL C13 and native O8CDD
50 pg/uL native 2,3,7,8-T4CDF
100 pg/uL native 1,2,3,7,8-P5CDF
100 pg/uL native 1,2,3,4,7,8-H6CDF
100 pg/uL native 1,2,3,4,6,7,8-H7CDF
150 pg/uL native O8CDF

6.2 Alumina: activate alumina (Fisher, 80-200 mesh) at 550 C overnight and deactivate with 1% w/w distilled water.

6.3 Acid silica gel: activate silica gel (Fisher, 60-200 mesh) at 150 C overnight. Add 50 g conc. H_2SO_4, about 5 g at a time, to 100 g silica gel, shake between additions and mix well.

6.4 Base silica gel: same as section 6.3 except add 35 g 1N NaOH instead of acid.

6.5 Sodium sulphate: granular, anhydrous, heat at 550 C overnight and store in a dessicator.

6.6 Solvents, pesticide residue quality, distilled in glass: toluene, hexane, benzene, ethyl acetate, dichloromethane, acetone, cyclohexane.

6.7 Carbon-fibre: shred 6 g of glass fibre filter paper (GA200, Toyo Roshi Co. Ltd.) in 100 mL of hexane and add 0.5 g of activated carbon (PX-21 Amoco Research Corp.). Shred mixture again with an ultrasonic dispersator.

6.8 Mercury: triple distilled (Canlab).

7.0 Procedure

7.1 Glassware washing

All glassware must be scrupulously cleaned before use. Wash glassware with detergent in hot water, rinse with copious amounts of hot water and rinse three times with acetone. Rinse with working solvent before using. Soak centrifuge tubes and micro vials in chromerge and rinse carefully before washing. It is important that micro vials and any glassware used in the final concentration steps be absolutely free from contaminants.

7.2 Preparation of samples

7.2.1 Fish samples

Homogenize sample with an ultrasonic dispersator if fish is whole. Mix with a spatula if fish is already homogenized.

7.2.2 Sediment samples

If sample is dry, sieve if necessary and mix well. If sample is wet, pour in clean aluminum weighing dish and air dry in fume hood. Moisture content can be

determined by weighing the dish before and after drying. Sieve sample and mix well.

7.3 Extraction of samples

7.3.1 Fish samples

Place approximately 75 g of sodium sulphate in a 250 mL beaker and add an accurately weighed 25 g sample of fish. Add another 75 g of sodium sulphate and mix well. Let stand for about an hour and grind sample to a powder using blender. Pour sample into extraction column, spike with 25 uL of surrogate standard (6.1A) and elute with 500 mL of 50% DCM/hexane. Concentrate the sample with a rotary evaporator until only lipids remain, transfer to centrifuge tube with 3 X 2 mL 50% DCM/hexane and adjust final volume to 4 mL or dilute to 0.5 g/mL of lipids if necessary. Proceed to 7.3 GPC cleanup.

NOTE: lipids content can be determined by making sure all of the extraction solvent is removed from the extract and weighing the round bottom flask before and after transfer to the centrifuge tube.

7.3.2. Sediment samples

Wash soxhlet apparatus, including thimble, by refluxing with toluene for a few hours. Accurately weigh 5 g of dry sediment in a 250 mL beaker. Add 40 g of sodium sulphate and mix well. Transfer the mixture to a extraction thimble and spike with 25 uL of surrogate standard (6.1A). Extract overnight with 300 mL toluene using soxhlet. Concentrate the sample just to dryness by rotary evaporation, dissolve the residue in 1-2 mL

50% DCM/hexane and proceed to 7.5 acid/base silica cleanup.

NOTE: If the sample is suspected of containing large amounts of sulphur, transfer the extract to a centrifuge tube, add approximately 0.5 mL of triple-distilled mercury and shake using a vortex mixer until the formation of a black precipitate ceases.

7.4 GPC cleanup

Flush injection loops and syringe with 50% DCM/hexane. Load fish extract onto loops, 4 mL/loop, using as many loops as necessary. Make sure settings for dump, collect, wash and terminal loops are correct before starting the run.

7.5 Acid/base silica cleanup

Plug the tip of a pasteur pipette with glass wool and add the following in the order specified: 0.5 cm sodium sulphate, 2 cm base silica, 4 cm acid silica, 0.5 cm sodium sulphate. Tap column gently to ensure even layering. Prewash column with 5 mL of 50% DCM/hexane. Transfer sample extract to the column with small washings and elute with 50% DCM/hexane. Collect 12 mL in a centrifuge tube. Concentrate the extract to 0.5 mL with nitrogen. Proceed to 7.6 alumina/carbon fibre cleanup.

7.6 Alumina/carbon fibre cleanup

Pack a stainless steel column with 1% alumina and wash with 40 mL of 1% DCM/hexane. Prewash the carbon fibre

column with 40 mL of toluene in reverse flow mode, switch to normal flow mode and wash with 40 mL of 50% DCM/hexane. With the flow of the column directed to waste, inject the sample extract and elute with 90 mL of 1% DCM/hexane. Connect an alumina column to a carbon fibre column and elute with 75 mL of 50% DCM/hexane. Disconnect the alumina column and elute the carbon column first with 40 mL of 10% benzene/ethyl acetate and then with 32 mL of 50% benzene/ethyl acetate. Reverse the flow of the carbon fibre column. Elute with 60 mL of toulene and collect in a 100 mL round bottom flask. This fraction contains dioxins and furans. Concentrate the sample with a rotary evaporator just to dryness and transfer to a centrifuge tube with 3 X 1 mL washings of toluene. Reduce the volume to about 100 uL with nitrogen and transfer to micro vial with small toluene washings. Concentrate to dryness with nitrogen and proceed to GC-MSD analysis.

7.7 GC-MSD analysis

Add 25 uL of the performance standard (6.1B) to a sample vial, cap and wash walls of vial by using vortex mixer. Inject 2 uL of the extract on the GC-MSD. Data integration and reporting is done automatically using the data acquisition system.

8.0 Calculations and Confirmation of Identity

8.1 Calibration

8.1.1 Tuning of the MSD is done automatically by running the autotune program.

8.1.2 The dioxins and furans calibration table is updated by running the quantitation standard (6.1C) and replacing the area values by the new ones. If the retention times change, they should also be replaced by the new values.

8.1.3 The quantitation standard should be analyzed at least twice a day when performing GC-MSD analysis. The values can be averaged and sample concentrations are recalculated based on averaged values.

8.2 Sample analysis

8.2.1 Sample analysis is carried out by monitoring, for each congener group over its specified window, the two most intense ions in the molecular cluster and the M-COCl ion for the natives, in addition to the two most intense ions in the molecular cluster for the corresponding C13 surrogate. The detection of the specified ions in the correct ratios and at the right retention times provides positive identification of the presence of a particular isomer in the sample.
Use is made of the quantitation and reporting software provided with the HP5970 data acquisition system.
The quantitation is based on the C13 internal standards which automatically corrects results for losses of material during clean-up and for chromatographic variations between injections.
After running a standard, the calibration table is updated and the system creates a response ratio (unlabelled/labelled) versus a concentration ratio calibration curve for each isomer specified in the table. The ratios found for the sample are then compared with the calibration curves and the

concentration of each specified dioxin or furan determined. Recoveries are determined by comparing the area values of the surrogates in the sample with those of the standard.

9.0 Precision and Accuracy

9.1 From method spikes, surrogate recoveries and performance standard calculated values, mean, standard deviation and coefficient of variance were determined for each of the dioxin parameters. No surrogates and spikes were used for furans.

9.2 For each batch of 10 samples, one blank and one spike each were run. Surrogate and performance standard were added to each sample before extraction and injection respectively.

9.3 Sediment

9.3.1 Method spikes

# of Spikes (n)	Parameters (C13)	Mean (%)	S.D. (%)	C.V. (%)
5	T4CDD	61	14.7	24.2
5	P5CDD	63	13.6	21.8
5	H6CDD	59	11.7	20.0
5	H7CDD	55	10.0	18.4
5	08CDD	52	21.6	41.6

9.3.2 Surrogates

# of Spikes (n)	Parameters (C13)	Mean (%)	S.D. (%)	C.V. (%)
15	T4CDD	81	11.0	13.6
15	P5CDD	80	14.8	18.5
15	H6CDD	77	12.2	14.9
15	H7CDD	75	20.3	26.9
15	O8CDD	73	21.5	29.5

9.3.3 Performance Standard

5	1,2,3,4-T4CDD	109	12.6	11.5

9.4 Fish

9.4.1 Surrogates

# Analysis (n)	Parameters	Mean (%)	S.D. (%)	C.V. (%)
20	T4CDD	74	12.8	17.3
20	P5CDD	77	13.6	17.6
20	H6CDD	80	16.5	20.5
20	H7CDD	82	16.7	20.5
20	O8CDD	74	18.4	25.1

9.4.2 Performance Standard

20	1,2,3,4-T4CDD	107	7.9	7.4

10.0 QA/QC

10.1 A method blank and a method spike are processed with each batch of 10 samples. The blank consists of 300 mL of the extraction solvent and is treated as a sample. The method spike is essentially a blank to which is added 25 uL of the surrogate standard. To be considered acceptable, the blank must not show any positive results or serious interferences. The method spike must show recoveries in the range of 40-130% for all surrogates.

10.2 The samples must show recoveries of all the surrogates in the range of 20-130%. Samples which do not meet this criterion are repeated. If poor recoveries are again obtained, it is assumed that the matrix is responsible and results are reported along with the recoveries.

10.3 The performance standard, added to each sample before injection, provides a means by which the success of the injection and the performance of the instrument can be evaluated. To be considered successful, the recovery of this standard must be 80-120%. Performance standard recoveries outside of this range are due to sample matrix interferences.

11.0 Remarks

11.1 It is recommended that a different carbon fibre column be used for fish and sediment samples. It was found that the efficiency of the carbon fibre column decreases dramatically after injecting heavily contaminated sediment or sludge samples. On the other hand, dozens of fish samples can usually be injected

before it becomes necessary to replace the carbon fibre column.

11.2 It is imperative that no carbon particles, from the carbon fibre column, get into the collection flask. This has the effect of lowering the recoveries of the higher chlorinated dioxins and furans homologues. When repacking the column, make sure the frits and seals are in good condition and leak free.

12.0 References

Afghan, B.K., J. Carron, P. D. Goulden, J. Lawrence, D. Leger, F. Onuska, J. Sherry, and R. Wilkinson. 1987. Can. J. of Chem. 65:1086- 1097.

Afghan, B.K. and R.J. Wilkinson. 1984. Cleanup and Isolation Procedure for the Analysis of Dioxins and Furans in Environmental Samples, National Water Research Institute Manuscript No. 112-AMD-3-84-BKA.

River Road Environmental Technology Centre. 1985. Analytical Method for the Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans in Samples from Municipal Solid Waste Incinerators.

Norstrom, R.J., M. Simon and M.J. Mulvihill. 1986. Intern. J. Environ. Anal. Chem. 23:267-287.

Smith, L.M., D.L. Stalling and J.L. Johnson. 1984. Anal. Chem. 56:1830-1842.

APPENDIX II

QUALITY ASSURANCE (QA)/QUALITY CONTROL (QC)

Laboratory QA/QC for Dioxins/Furans

The method for the determination of dioxins and furans (Appendix I), describes details of laboratory QA/QC. The laboratory QA/QC results are shown in Tables IIa and IIb. The spikes for fish showed better recoveries than the spikes for sediments. This was expected, as the sediment matrix was more complex.

In addition to the regular internal quality control, the laboratory also participated in the "Three Mill Study Round Robin" for biological tissue concurrently with the analysis of fish samples. National Water Quality Laboratory results for this round robin compared very well with all participating laboratories (Whittle 1989).

Sample QA/QC

Due to difficulties in obtaining reference materials for QA/QC, no blind samples with a known concentration of dioxin/furans were submitted for analysis. However, blind triplicate samples for both sediment and fish were submitted to the laboratory and the results are shown in Tables IIc and IId respectively.

Sediment

Sample numbers A1, A2 and A3 are subsamples of a composite collected from one location. The sample was subdivided into subsamples in the field. Similarly, sample numbers B1, B2 and B3 were subsamples of another composite. Samples A1 and B1 were analyzed by the laboratory about four months earlier than samples

A2, A3, B2 and B3. Results in Table IIc indicate that subsamples analyzed at the same time (A2, A3 and B2, B3) show good reproducibility. However, samples analyzed four months apart (A1 versus A2 and A3; B1 versus B2 and B3) showed greater variance, especially in concentration of T4CDDs. This may be partly due to the fact that the samples containing small pieces of wood chips and a large amount of fibrous material were difficult to subsample homogeneously.

Fish

As in the case of sediment, samples C1, C2 and C3 are subsamples of one composite and D1, D2 and D3 are subsamples of another (Table IId). Samples C1 and D1 were analyzed approximately three months earlier than samples C2, C3, D2 and D3. Both sets of samples showed good reproducibility for dioxins/furans. However, lipid content exhibited a large variance between samples. During analysis, the laboratory personnel noticed separated oil in samples C2, C3, D2 and D3. Perhaps mixing with a spatula prior to weighing a subsample for analysis of lipids was not adequate when the oil is separated, and a further homogenizing step should be added.

Reference

Whittle, D.M. 1989. Division Manager, Ecotoxicology Division. Great Lakes Laboratory for Fisheries and Aquatic Sciences, Fisheries and Oceans Canada, Burlington, Ontario. Personal Communication.

TABLE IIa. ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON BED SEDIMENTS, EXPRESSED AS PERCENT RECOVERY

	SURROGATE SPIKE					PERFORMANCE STANDARD
SITE LOCATION	Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD	
Mackenzie Pulp	66	64	67	74	47	102
Mills	61	67	64	64	69	120
Upstream	76	77	79	59	62	90
Finlay Forest	72	76	63	66	45	126
Industries Ltd.	69	61	45	40	29	116
Downstream	54	49	35	35	34	102
Fletcher Challenge	67	72	70	72	53	86
Canada Ltd.,	80	70	76	64	125	124
Mackenzie Pulp	75	70	57	48	33	85
Division (B.C. Forest Products) Downstream						
Prince George	90	78	56	47	48	96
Pulp Mills	97	98	97	93	95	100
Upstream	101	94	85	71	64	97
Northwood Pulp	89	78	55	41	30	93
and Timber	72	73	68	51	58	76
Downstream	83	82	74	59	55	89
Canfor Prince	72	60	47	37	34	88
George Pulp and	55	14	8	27	61	95
Paper Mills	28	30	24	22	18	89
Downstream						
Method Spike	62	68	67	62	57	96
Quesnel Pulp Mills	94	110	105	118	84	109
Upstream	84	92	85	111	93	106
	90	99	92	103	95	114
Quesnel River Pulp	87	98	74	90	87	105
Co.	93	68	58	51	69	107
Downstream	88	64	62	65	75	100
Cariboo Pulp and	86	94	88	67	50	117
Paper	116	125	120	89	48	107
Downstream	108	111	92	63	40	100
Method Spike	77	77	73	64	54	115

TABLE 11a (CONTINUED)

SITE LOCATION	SURROGATE SPIKE					PERFORMANCE STANDARD
	Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD	
Weyerhaeuser Canada Ltd. Upstream	75	12	ND	38	33	96
	76	77	73	58	32	119
	64	66	70	67	65	109
Weyerhaeuser Canada Ltd. Downstream	75	68	46	29	18	106
	117	110	71	26	18	150
	74	77	79	60	46	106
Power Consolidated * (China) Pulp Inc., (Celgar) Downstream	73	65	5	10	23	90
	83	60	6	10	20	108
	94	54	17	11	23	94
Method Spike	67	68	55	49	83	100
Power Consolidated * (China) Pulp Inc., (Celgar) Upstream	80	61	45	54	34	93
	81	79	71	76	72	90
	119	99	54	67	44	104
Crestbrook Forest Industries Ltd., Pulp Division Upstream	60	56	58	60	69	80
	102	59	23	43	42	102
Crestbrook Pulp Industries Ltd., Pulp Division Downstream	111	95	73	46	37	105
	75	78	76	70	62	93
	92	93	84	68	51	97
	87	88	69	56	40	105
Method Spike	37	41	43	40	42	100
Method Blank	ND	ND	ND	ND	ND	109

* In Table 3, Power Consolidated Upstream results are presented before Power Consolidated Downstream results.

ND denotes not detected.

TABLE IIb. ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON FISH MUSCLE TISSUE, EXPRESSED AS PERCENT RECOVERY

SITE LOCATION	FISH SPECIES	SURROGATE SPIKE					PERFORMANCE STANDARD	METHOD SPIKE, METHOD BLANK REFERENCE *
		Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD		
Mackenzie Pulp Mills Upstream	Catostomus macrocheilus	68	66	64	57	50	105	4,-
	Mylocheilus caurinus	80	79	81	80	64	98	4,-
	Prosopium williamsoni	88	87	90	85	76	108	1,A
Finlay Forest Industries Ltd. Downstream	Catostomus macrocheilus	69	78	84	87	86	97	3,C
	Coregonus clupeaformis	95	96	95	89	90	108	4,-
	Lota lota	72	70	75	72	60	92	4,-
Fletcher Challenge Canada Ltd., Mackenzie Pulp Division (B.C Forest Products) Downstream	Catostomus macrocheilus	93	99	101	101	94	121	4,-
	Coregonus clupeaformis	58	79	87	92	86	114	4,-
	Lota lota	80	79	76	69	48	116	4,-
Prince George Pulp Mills Upstream	Catostomus catostomus	80	64	77	67	50	125	2,B
	Catostomus macrocheilus	52	44	45	44	35	96	2,B
	Ptychocheilus oregonensis	65	57	54	46	38	114	2,B
Northwood Pulp and Timber Downstream	Catostomus macrocheilus (a)	82	89	90	81	72	98	1,A
	Catostomus macrocheilus (b)	56	53	53	48	41	99	2,B
	Prosopium williamsoni	57	66	73	74	65	114	1,A

TABLE IIb (CONTINUED)

SITE LOCATION	FISH SPECIES	SURROGATE SPIKE Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD	PERFORMANCE STANDARD	METHOD SPIKE, METHOD BLANK REFERENCE *
Canfor Prince George Pulp and Paper Mills Downstream	Catostomus columbianus	76	69	68	62	57	98	2,B
	Catostomus macrocheilus	76	72	69	64	51	115	2,B
	Prosopium williamsoni	80	85	89	83	74	109	2,B
Quesnel Pulp Mills Upstream	Catostomus columbianus	66	57	52	45	32	95	2,B
	Catostomus macrocheilus	87	84	77	79	53	94	1,A
	Mylocheilus caurinus	73	68	70	68	57	113	4,-
Quesnel River Pulp Co. and Cariboo Pulp and Paper Downstream	Catostomus columbianus	82	65	54	70	69	101	4,-
	Catostomus macrocheilus	78	79	83	76	69	99	1,A
	Prosopium williamsoni	81	83	88	84	71	110	4,-
	Salvelinus malma	83	92	99	101	91	112	3,C
Weyerhaeuser Canada Ltd. Upstream	Catostomus macrocheilus	77	92	96	98	96	115	3,C
	Prosopium williamsoni	89	91	91	85	82	96	3,C
	Salvelinus malma	80	83	84	77	71	106	3,C
Weyerhaeuser Canada Ltd. Downstream	Catostomus macrocheilus	75	84	85	66	62	108	3,C
	Prosopium williamsoni	84	66	65	75	84	107	3,C
	Ptychocheilus oregonensis	82	81	79	70	60	102	3,C
Power Consolidated (China) Pulp Inc., (Celgar) Upstream	Catostomus macrocheilus	76	77	76	71	66	94	1,A
	Coregonus clupeaformis	86	76	70	62	53	107	1,A
	Ptychocheilus oregonensis	77	85	96	99	102	95	3,C

TABLE IIb (CONTINUED)

SITE LOCATION	FISH SPECIES		SURROGATE SPIKE Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD	PERFORMANCE STANDARD	METHOD SPIKE, METHOD BLANK REFERENCE *
Power Consolidated (China) Pulp Inc., (Celgar) Downstream	Catostomus macrocheilus		74	62	63	55	49	107	1,A
	Coregonus clupeaformis	(a)	87	90	96	90	71	118	1,A
	Coregonus clupeaformis	(b)	88	92	95	91	87	100	3,C
Crestbrook Forest Industries Ltd., Pulp Division Upstream	Catostomus macrocheilus		91	98	100	99	94	110	3,C
	Prosopium williamsoni		88	96	105	107	99	95	3,C
	Salmo clarki		84	81	80	62	70	108	3,C
Crestbrook Pulp Industries Ltd., Pulp Division Downstream	Catostomus macrocheilus	(a)	64	77	86	112	89	109	3,C
	Catostomus macrocheilus	(b)	45	50	43	69	65	103	3,C
	Prosopium williamsoni		77	85	85	74	66	90	1,A
* Method Spike:		1	110	114	104	94	104	113	
		2	75	91	92	89	77	114	
		3	79	85	86	77	66	102	
		4	67	69	74	72	60	108	
* Method Blank:		A	ND	ND	ND	ND	ND	105	
		B	ND	ND	ND	ND	ND	109	
		C	ND	ND	ND	ND	ND	101	

ND denotes not detected

TABLE IIc. RESULTS OF REPLICATE BED SEDIMENT SAMPLES

SAMPLE NO.	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g dry wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
A1	62.1	L15	L15	L20	L30	L50	572	2077	3227	51	34	L40	L75
A2	70.1	68.2	68.2	L20	L30	243	208	2064	3023	L15	L25	L40	L75
A3	70.1	66.5	66.5	L20	L30	123	252	2256	3210	L15	L25	L40	L75
B1	32.4	L15	L15	L20	L30	L50	L75	3168	4521	L15	L25	L40	L75
B2	32.6	83.3	83.3	L20	L30	L50	L75	2210	3383	L15	L25	L40	L75
B3	30.2	78.9	78.9	L20	L30	L50	L75	2206	3168	L15	L25	L40	L75

L denotes less than specified detection limit.

TABLE IId. RESULTS OF REPLICATE FISH MUSCLE TISSUE SAMPLES

SAMPLE NO.	FISH SPECIES	LIPID CONTENT (% wet wt.)	MOISTURE CONTENT (%)	DIOXIN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total O8CDD	FURAN CONCENTRATION (pg/g wet wt.) 2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
C1	Catostomus macrocheilus (largescale sucker)	1.6	79.3	11.7	11.7	L3	L5	L10	L15	156	156	L3	L5	L10	L15
C2		5.7	79.2	16.7	16.7	L3	L5	L10	L15	259	259	L3	L5	L10	L15
C3		4.9	79.2	15.4	15.4	L3	L5	L10	L15	257	257	L3	L5	L10	L15
D1	Catostomus macrocheilus (largescale sucker)	1.1	80.1	L2	L2	L3	L5	L10	L15	38.6	38.6	L3	L5	L10	L15
D2		4.2	78.3	L2	L2	L3	L5	L10	L15	37.3	37.3	L3	L5	L10	L15
D3		3.3	78.3	L2	L2	L3	L5	L10	L15	35.4	35.4	L3	L5	L10	L15

L denotes less than specified detection limit.